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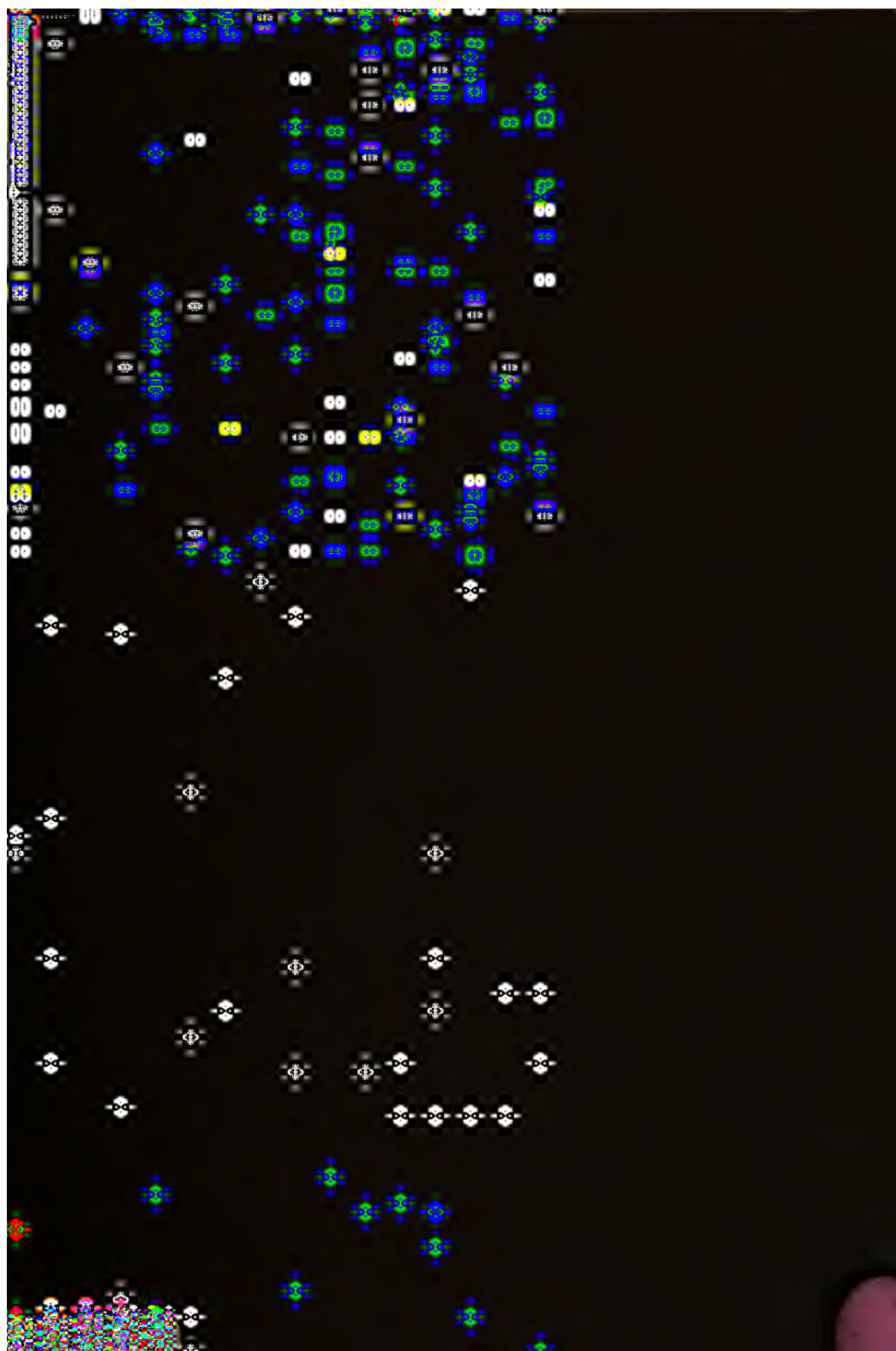
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A MANUAL OF QUANTITATIVE CHEMICAL ANALYSIS

FOR THE USE OF STUDENTS

BY
FREDERICK A. CAIRNS, A.M.

*Late Instructor in Analytical Chemistry, School of Mines
Columbia College*

*THIRD EDITION
REVISED AND ENLARGED*

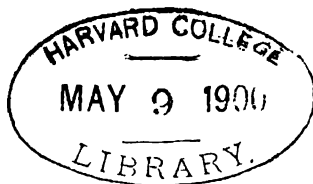
BY
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TO
PROFESSOR CHARLES F. CHANDLER,
THE FRIEND, TEACHER, AND CO-LABORER OF THE
AUTHOR, THIS BOOK IS, IN ACCORDANCE
WITH THE AUTHOR'S
WISHES,
DEDICATED.

AUTHOR'S PREFACE TO THE FIRST EDITION.

THIS manual is designed to assist beginners in the practice of quantitative analytical chemistry.

The aim is, by explaining some of the more serious obstacles to successful analysis, to teach thoughtfulness and caution, and by giving very explicit directions in the earlier part of the course, to induce habits of precision, and impart a sufficient amount of knowledge of chemical manipulation to enable the student to proceed without further leading.

The system adopted is to teach at first the determination, individually, of the constituents of compounds, composed of elements which will afterward, very frequently, be found variously associated, particularly in mineral analysis; and then to teach the quantitative separation of these elements, in the analysis of compounds containing a number of them; advancing, step by step, from the analysis of compounds of similar character to the analysis of more complicated ones, involving a knowledge and application of what has preceded.

In addition to the series of what may be called strictly mineral have been added a number of analyses of substances of an organic character, found in commerce, which will give the student an insight into the work which will probably be required of him as a practical chemist.

The range of these is necessarily restricted, as it is desired to keep the work within the limits of a simple handbook.

The writer has avoided giving numerous methods of analysis of

the same substance, but has selected those which he knows to be good, and which he believes to be the best.

The instructor is expected to enlarge upon the instructions given here, and the student to study other works of a more elaborate character. Success requires knowledge of theoretical chemistry and quantitative analysis.

EDITOR'S PREFACE.

SINCE this book was first published (1880) important changes have been made in the practice of analytical chemistry, and therefore, by this time, a very thorough revision has become necessary.

In revising, many of the chapters had to be rewritten, and some additional chapters have been found to be necessary. In this work, the endeavor has been made to retain as much as possible the features of the original work and the lines laid down by the author. The prominent idea was that the book is primarily intended for students not yet perfectly versed in the practice of Analytical Chemistry, so that although it may be of service for reference to Analytical Chemists, they may find it to contain many suggestions which they would regard as of elementary character.

The aim has been to give descriptions and directions for such methods as are generally pursued in most analytical laboratories, with brief references to the theory of other methods, that the student may have presented to him one or two plans of procedure which find acceptance at the present time, and at the same time suggestions of other plans which may in time lead to modifications of our present methods. In any case, these will help to broaden the students' knowledge of the chemical relations of the substances with which he has to deal.

Extensive and radical changes have been made in the science and practice of Quantitative Proximate Analysis since the death of Mr. Cairns, and it has therefore been decided to cut out all of the chapters in former editions relating to that branch of the subject, and to retain only what was always the chief feature of his work, namely, Mineral Analysis.

In the Appendix, containing the tables, has also been introduced

the paper on Properties and Precipitates, etc., prepared by the editor for the use of his students as an adjunct to their work with this book, and first published in the *School of Mines Quarterly*, vol. XII., pp. 235 and 297. Some few additions and alterations have been made.

A description of a very convenient form of Burette-filler has also been inserted.

Mention should be made of many of the graduates of the School of Mines and others who, on account of their former personal relations with Mr. Cairns or with the editor, have kindly assisted by responding to requests for advice, criticism, or suggestion. To name each and every one would be a difficult matter, and the editor deems it best to content himself with this general acknowledgment.

ELWYN WALLER.

July, 1896.

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INTRODUCTION.

As gravimetric analysis is effected by separating, one by one, the different constituents from a solution containing a known amount of the substance to be analyzed by adding other substances, called reagents, which will form with the constituents to be determined compounds insoluble in the surrounding fluid, care must be taken not to use excessive quantities of these reagents.

Take, as an illustration, the analysis of limestone. After decomposing the stone and separating the silica, which is done in acid solution, the solution is made alkaline with ammonia, by which means the ferric and aluminic hydrates, being insoluble in ammonia, are precipitated; the lime is then precipitated, by the addition of ammonium oxalate, as calcium oxalate, a compound insoluble in ammonia; the magnesia is then precipitated from the residual fluid as magnesium ammonium phosphate (by the addition of sodium phosphate), a compound insoluble in ammonia.

This is the outline of the method of analysis. Suppose an excessive quantity of hydrochloric acid to have been used in the first instance, a large quantity of ammonia would be required to precipitate the iron and alumina, and consequently a large quantity of ammonium chloride formed in the solution. If, in addition to this, an unnecessary quantity of ammonium oxalate were used, it would be found impossible to complete the analysis successfully

without danger of loss and great waste of time and labor. The danger of loss always accompanies prolonged operations in chemistry ; the waste of time would be consequent upon the necessity of evaporating to dryness to expel the large amount of ammonium chloride, in the presence of which the magnesium could not be completely precipitated (an operation involving considerable loss of time and possibly of substance). Finally, after all this waste of time and labor, the presence of other salts, not volatilized by heat, would render it impossible to concentrate the fluid to the proper point for the thorough precipitation of the magnesium as phosphate, it being somewhat soluble in large amounts of fluid. Such difficulties as these can in nearly all cases be avoided by using no more of a solvent (acid or alkaline) than is necessary, and no more of a precipitant than is required to effect complete precipitation, or, in other words, by avoiding excessive use of reagents in all cases.

The expressions "soluble" and "insoluble" used in works on analytical chemistry are frequently misunderstood by students, being taken by them in an absolute and not in a relative sense. The terms are intended to signify that for practical purposes, with a moderate bulk of solution, a given substance may be regarded as soluble or insoluble : not that it is *soluble* to an indefinite extent, or absolutely *insoluble* in an unlimited quantity of water or other menstruum. Extreme cases of that kind do not, in fact, exist.

A knowledge of the use of solvents can be attained by studying the solubility of substances, and a knowledge of the amount of reagents to be used by simple stoichiometrical calculations. The student should bear in mind that water is also a reagent, and that excessive use of it is to be condemned. At the end of this chapter will be found a table giving the amount of the different elements, etc., precipitated by 1 c. c. of a solution of each of the reagents most commonly used.

Before beginning an analysis of any complexity, a plan should be adopted and well studied. In many cases, tabular schemes will be found very useful, as they enable the chemist to see at a glance the relative bearing of each part of an analysis, and refresh the memory without loss of time.

MEASURING.

Vessels for the measurement of the bulk of *solutions* only are here referred to, such as beakers, flasks, pipettes, burettes, etc.

Beakers.—For roughly approximate measurements, the capacity of the ordinary (lipped) beakers may be used. When filled to such a point that the surface of the liquid nearly approaches the curvature of the brim, the capacities are *about* as follows :

No. 1	Beaker.....	100 c. c.
No. 2	"	200 c. c.
No. 3	"	300 to 350 c. c.
No. 4	"	500 c. c.
No. 5	"	750 to 800 c. c.
No. 6	"	1000 c. c.

A tolerably close estimate of the volume of any solution with which one may be working may be made by filling another beaker of the same number, size, and pattern with water to the same depth as nearly as can be estimated by the eye, and then measuring the volume in the "dummy" by means of graduated flasks.

Flasks.—Of these it is well to have a series which will deliver respectively 50 c. c., 100 c. c., 150 c. c., 200 c. c., 250 c. c., 300 c. c., 500 c. c., and 1000 c. c. In most cases, it is not of so much importance that they should be absolutely accurate as to capacity, as that they should bear an accurate relationship to each other, as otherwise it will be impossible to divide solutions correctly, a matter of the greatest importance in quantitative analysis. If it is desired to standardize a flask with great precision, it can be done by counterpoising it on a balance with any kind of weight

that is convenient, adding weights to those on the balance to an amount corresponding to the capacity of the flask, adding the proper amount of water, and marking the neck of the flask. As an illustration, we will suppose that it is desired to prepare a 50 c. c. flask. Select a flask with a narrow neck, in which the water will rise about half-way, upon introducing about 50 c. c. of it; dry the flask thoroughly,* inside and out, place it upon the pan of a balance, counterpoise it with any convenient weight, add to the weight 49.9405 gms., and introduce into the flask distilled water of 16° C., until perfect equilibrium is produced (after drying the neck of the flask above the water-line). Then mark the neck of the flask, which must stand perfectly level, where it is intersected by the horizontal plane coinciding with the bottom of the meniscus. This mark is what is called the "holding" or "containing" mark. Of course, when the contents of the flask are poured out, some of the fluid will adhere to the sides, and it will fail to deliver 50 c. c. It becomes necessary, therefore, to establish a point to which the flask must be filled to enable it to deliver 50 c. c. To do this, fill the flask with water, empty it, counterpoise it as before, together with the fluid adhering to the inside, being careful that the outside is dry, replace the weights amounting to 49.9405 gms., introduce distilled water of 16° C. until equilibrium is restored as before, and mark the neck of the flask where it is intersected by the horizontal plane tangent to the bottom of the

* To dry a flask inside: After washing and emptying out the water, rinse once or twice with strong alcohol to remove the last few drops of water, then rinse once or twice with ether to remove the last portions of alcohol, and finally vaporize and expel the ether by a current of air from the blast connection, *not from the lungs*, since the moisture of the breath would condense and defeat one's object.

Drying out in this manner is unnecessary in the case of burettes, etc., intended to be filled with standard solutions. In such cases it suffices to rinse out the burette, etc., with a few c. c. of the standard solution, run that to waste, and then fill with the standard solution for use.

meniscus. This mark is what is called the "delivery" mark.

In this way, all the flasks required can be prepared with great accuracy. If, however, an accurately measured flask is at hand, another of twice or thrice the capacity can readily be prepared by filling the smaller flask to the delivery mark with water of 16° C., emptying it into the larger flask, previously dried, repeating until the desired volume is reached, and marking upon the neck of the flask the holding point. By repeating the operation upon the wet flask, the delivery mark can be established.

With small flasks of 100 c. c. or less, the width of the meniscus is often the difference between the "holding" and "delivery" mark; *e. g.*, many 100 c. c. flasks will *hold* 100 c. c. when the mark is at the *top* of the meniscus, and will *deliver* 100 c. c. when the mark is at the *bottom* of the meniscus.

Flasks can also be prepared with great ease by means of a pipette the capacity of which is known. If, for instance, a pipette which is known to deliver 50 c. c. is at hand, all that is necessary to prepare a 200 c. c. flask is to dry it, run into it 4 pipette-fulls of water of 16° C., and mark the proper point on the neck as the holding mark; and determine the delivery mark by repeating on the wet flask.

For many purposes the use of flasks holding or delivering a definite number of c. c. is unnecessary. For instance, to obtain a certain fraction of a solution, it suffices to take a flask of convenient capacity, make a mark on the neck, and fill to that mark a definite number of times; then, after mixing, one flask-full will represent a definite fraction of the solution. For example: Suppose one-fifth of a solution (roughly estimated as 200 c. c. or less) is required. Select a flask having a capacity of 45 to 60 c. c., and make a mark on the neck. Fill to the mark with some of the solution, and pour into a *dry* beaker. Repeat this four times. The last filling should exhaust the solution, the rinsings being used to make five flasks-full. After *thorough*

mixing and rinsing the flask *at least once* with the mixed solution, one flask-full will represent one-fifth of the material in the original solution. The rinsings of the measuring flask may be divided by guess. Measurements of this sort should always be made at the *ordinary temperature* of the laboratory.

Pipettes.—These can usually be purchased cheaply, so that ordinarily there is no occasion to make or graduate them. Their accuracy should, however, always be verified. This is commonly done by filling them up to the proper mark with water of 16° C., running this water into a weighed flask, and weighing the amount delivered. This should be nearly the same number of grammes as the pipette is supposed to contain in cubic centimetres, a slight difference being made for the expansion of water between 0 and 16° C. One cubic centimetre of water at 16° C. weighs 0.9988 gms.

A pipette must always be filled by suction to above the mark, with the liquid to be measured; then, by closing the top with the dry finger, the liquid may be allowed to run slowly out, until the lower part of the meniscus is at the line. It will then (if correct) deliver the number of c. c. marked upon it. Pipettes being used for *delivery only*, have no holding mark, as with flasks. In running the liquid out of the pipette, touch the tip lightly against the side of the vessel into which it is delivering, until no more runs out. Never blow out the last drop, since that renders the measurement inaccurate.

If a burette is taken, the accuracy of which has been verified by weighing the amounts delivered, as referred to above, the accuracy of any number of pipettes may be readily tested, by first filling them with water, running it out so as to leave the same amount adhering to the glass as when in use, and then closing the tip with the finger, and running in water of 16° C. from the burette. For this work, the burette should be provided with a fine-pointed delivery-jet.

The same method will serve for graduation, if that is necessary. (See Thorpe's "Quant. Anal." pp. 112 *et seq.*) Students should also have a few small test glasses holding from 10 to 15 c. c., and graduated to c. c. These will be found more convenient for controlling the use of reagents than pipettes, and for most purposes are sufficiently accurate.

It is also convenient to have on hand a few glass tubes each six or eight inches long, drawn to a tip like a pipette, for obtaining one or two drops of a reagent, passing H_2S , CO_2 , etc.

For measuring of gases, read Fresenius, who extracts from the best authorities, such as Bunsen, Regnault, and others.

WEIGHING.

As quantitative analysis requires, in addition to the separation of the constituents of a substance, the determination of their relative quantity, accurate weighing is absolutely necessary. A good balance is, of course, essential. For discussions of the principles of the balance, the student is referred to such works as that of Fresenius, as space will not allow their being introduced here. Rules for weighing are all that are admissible. Those given by Fresenius are introduced here.

1. The safest and most expeditious way of ascertaining the exact weight of a substance is to avoid trying weights at random; instead of this, a strictly systematic course ought to be pursued in counterpoising substances on the balance. Suppose, for instance, we want to weigh a crucible, the weight of which subsequently turns out to be 6.627 gms.; we place 10 gms. on the other scale against it, and we find this too much; we place the weight next in succession, *i. e.*, 5 gms., and find this too little; next 7, too much; 6, too little; 6.5, too little; 6.7, too much; 6.6, too little; 6.65, too much; 6.62, too little; 6.63, too much; 6.625, too little; 6.627, right.

I have selected here, for the sake of illustration, a most complicated case; but I can assure the student of quantitative analysis that this systematic way of laying on the weights will, in most instances, lead to the desired end in half the time required when weights are tried at random. After a little practice, a few minutes will suffice to ascertain the weight of a substance to within the tenth of a milligramme, provided the balance does not oscillate too slowly.

2. The milligrammes and fractions of milligrammes are determined by a centigramme rider (to be placed on or between the divisions on the beam) far more expeditiously and conveniently than by the use of the weights themselves, and at the same time with equal accuracy.

3. Particular care and attention should be bestowed on entering the weights in the book. The best way is to write down the weights first by reference to the blanks or gaps in the weight-box, and to control the entry subsequently by removing the weights from the scale, and replacing them in their respective compartments in the box. The student should, from the commencement, make it a rule to enter the number to be deducted in the lower line; thus, in the upper line, the weight of the crucible + the substance; in the lower line, the weight of the empty crucible.

4. The balance ought to be arrested every time any change is contemplated, such as removing weights, substituting one weight for another, etc., etc., or it will soon be spoiled.

5. Substances (except, perhaps, pieces of metal, or some other bodies of the kind) must never be placed directly upon the scales, but ought to be weighed in appropriate vessels of platinum, silver, glass, porcelain, etc., never on paper or card, since these, being liable to attract moisture, are apt to alter in weight. The most common method is to weigh, in the first instance, the vessel by itself, and to introduce subsequently the substance into it; to weigh

again, and subtract the former weight from the latter. In many instances, and more especially where several portions of the same substance are to be weighed, the united weight of the vessel and of its contents is first ascertained; a portion of the contents is then shaken out, and the vessel weighed again, the loss of weight expresses the amount of the portion taken out of the vessel.

6. Substances liable to attract moisture from the air must be weighed invariably in closed vessels (in covered crucibles, for instance, or between two watch-glasses, or in a closed glass tube); fluids are to be weighed in small bottles with glass stoppers.

7. A vessel ought never to be weighed while warm, since it will in that case invariably weigh lighter than it really is. This is owing to two circumstances. In the first place, every body condenses upon its surface a certain amount of air and moisture, the quantity of which depends upon the temperature and hygroscopic state of air, and likewise on its own temperature. Now, suppose a crucible has been weighed cold at the commencement of the operation, and is subsequently weighed again while hot, together with the substance it contains, and the weight of which we wish to determine. If we subtract, for this purpose, the weight of the cold crucible, ascertained in the former instance, from the weight found in the latter, we shall subtract too much, and consequently we shall set down less than the real weight of the substance. In the second place, bodies at a high temperature are constantly communicating heat to the air immediately around them; the heated air expands and ascends, and the denser and colder air, flowing toward the space which the former leaves, produces a current which tends to raise the scale-pan, making it thus appear lighter than it really is.

These rules may be briefly summarized thus:

1. Put on the heaviest weights first.
2. Use the rider for differences under 10 milligrammes.*

*Most analytical balances are now provided with riders weighing 12 mgs., the beams being graduated accordingly. Some, however, are constructed for

3. Record the weight by noting the gaps in the weight-box. Check off in replacing.

4. Arrest the balance when changing weights (of over 500 mgs.).

5. Allow nothing but glass, metal, or porcelain in contact with the scale-pans.

6. Weigh hygroscopic substances covered.

7. Do not weigh substances or articles while warm.

It is further recommended to weigh the material taken for analysis *directly* in the vessel in which it is to be treated, wherever that is possible, *e. g.*, if it is to be treated with water or acids, use a light flask or beaker (tared). If it is to be fused, weigh out in a (tared) crucible.

The weight of material used may be taken *directly*, as already suggested, or by difference; *i. e.*, a corked tube or flask containing perhaps 10 or 20 gms. of the material is weighed, and then a convenient amount is taken out for analysis, and the tube or flask corked and weighed again. This method is advantageous in the case of hygroscopic substances.

To decide when the article is exactly counterpoised, some simply press the spring attached to the pan arrests, and then observe whether the indicator needle remains at the zero of the scale for a few seconds (10 or more). The ordinary method, however, is "by oscillation," causing the beam to swing gently, and then noting whether the needle passes over the same number of divisions on each side of the zero-mark.

riders of other weights,—10 mgs. (or for short beam-balances 6 mgs.). An inspection of the graduations on the beam will at once decide the point. (The twelfth or, as the case may be, the tenth (or sixth) division will coincide with the knife-edge from which the pan depends.) The error incident to the use of a 10 m. g. rider on a 12-division beam, or *vice versa*, is apparent.

FILTERING AND BEAKERS, ETC., WASHING.

Lipped beakers are always preferable. In pouring from a beaker, the stream should be always poured against a glass rod. No grease is required on the under side of the lip, if it is properly formed. The under side of the lip should always be dry. Rubbers on the rods should only be used to clean vessels. In filtering, the rods should have no rubbers on them, as it may introduce organic matter into the solutions, which may cause error in the work.

The length of the rods used should be proportioned to the size of the beaker employed. A rod of suitable length, when placed in the beaker for which it is adapted, should reach from the edge of the *lip* diagonally across to the lowest part of the beaker on the opposite side.

When a vessel holding several litres is to be heated, as it may be fractured by the great weight of fluid, if the bottom rests unevenly upon its support in heating, sand may be used as a support. In other cases, the use of sand is objectionable. It requires a longer time to heat a vessel standing upon sand, and the sand is very liable to adhere to the bottom of the vessel, and from it drop into the analysis.

The filter-paper used should be free from starch, which otherwise may introduce a disturbing influence into the work, the more objectionable because often unsuspected. Munktell's Swedish filter-papers supplied in sheets is usually nearly if not quite free from starch. The cut papers of the same brand, however, contain starch. If the filter-papers show a blue coloration when wetted with a very dilute *aqueous* solution of iodine, they should be washed thoroughly with boiling water in the funnel before use.

Except in the case of filter-papers which have been treated with hydrofluoric acid followed by hydrochloric, some allowance must be made for the ash of the filter-

paper after ignition. The amount differs, according as an acid or an alkaline solution has passed through the paper. Thus, for the Swedish filter-paper bearing the water-mark J. H. Munktell, the allowance is :

No.	Diameter in cm.	Acid.	Alkaline.
1	7	0.0004 gm.	0.0014 gm.
2	9	0.0007 "	0.0027 "
3	11	0.0011 "	0.0043 "
4	13	0.0016 "	0.0062 "

In the nature of things these can only be averages determined by treating 10 or 20 papers of each size with acid or alkali, washing thoroughly, and incinerating. It is therefore always advisable to use the smallest filter possible in every case. The theory is, that the acid removes something, whereas the alkaline solution does not, so that if a neutral solution has passed through the paper, the allowance made is that for alkaline ash, and if the paper has been subjected to the action of both acid and alkali, the acid ash is taken. Caustic (fixed) alkalis and alkaline earths, also some salts, are often retained by the cellulose of the paper with great persistency, requiring extreme care in washing. This point emphasizes the advantage of using ammonium salts when possible as reagents, the ammonium salts being volatilized on ignition.

In filtering, the filter should always be accurately fitted to the funnel, and the funnel adapted to the size of the filter, always using the smallest filter that will allow a proper washing of the contents. The larger the filter, the more washing it requires, and the greater the liability to error in allowing for the weight of the ash.

For filtration with the aid of a filter-pump, it is necessary to use something to support the point of the filter. A platinum cone accurately fitted to the funnel is often used, but a more convenient (and inexpensive) device consists in a bit of muslin folded as a filter-paper. Boiling the muslin in two or three changes of water will suffice to remove from it the starch or other soluble material which would

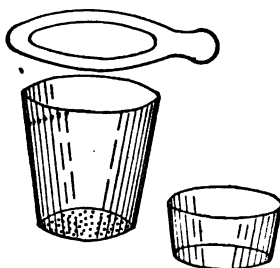
be objectionable. In filtering by this means it is not advisable to use too strong a suction, or the precipitate may become so densely packed as to prevent the liquid from running through.

Some substances, as gelatinous precipitates, etc., are most rapidly filtered out by giving them a large filtering surface and *not* applying suction. One device for this purpose consists in hanging a few small glass-rods in the funnel, over which the filter-paper is placed. With most granular precipitates a closely-fitting filter-paper is better, the solution completely filling the stem of the funnel. By attaching a slender tube about a yard long to the stem of the funnel the rapidity of filtration may be increased, provided the tube is kept full of liquid (in cases where a filter-pump is not available). The suction caused by the fall of that column of liquid is likely, however, to tear the filter-paper unless it is supported by a platinum or muslin cone.

It is always difficult to completely wash out any part of the filter-paper which is not against the glass of the funnel. This constitutes a serious objection to the use of plaited filters in many cases. When, however, the solution is very dilute, or other conditions favor, a plaited filter is of advantage as giving a larger filtering surface. To prepare a plaited filter, fold the (round) filter-paper in halves, then crease it sharply at the quarter, then at the eighths, having all of these folds bending the same way. Then put between each of these creases a crease in the opposite way. Do not attempt to make these creases very sharp near the point of the filter, as that may weaken or break the paper at that point. When all the creases have been made, open the paper completely and gather it into a star in the hand. Then thrust the point of the filter *into the stem* of the funnel, that the channels for the flow of the filtrate may be maintained. The filter-paper now stands stiffly in the centre of the funnel. Then pour in water, or the solution, and the paper will soften and fall against the sides of the funnel, against which only the points of the

“star” should rest. If the precautions described have been neglected the paper will bulge out under the pressure of the liquid, and the advantage of the plaited filter will be lost.

The Gooch crucible, a platinum crucible with a perforated bottom, is of great service in filtering by the aid of suction. One may use a paper in it if desired. In that case the paper should be cut (usually by a five-cent nickel coin) so as to exactly cover the bottom. The edges of the paper should not extend against the sides, or they will buckle into folds and the filtering surface will be spoiled. If asbestos



is used, the asbestos should be first shredded, then mingled with water, and the very fine particles which remain suspended poured off. After half a dozen washings of this kind, stir the fibre up with water and pour some into the Gooch. *Then*, and not until then, start the suction to bring the asbestos into place. Another charge of asbestos—forming another layer—may sometimes be advisable. If the pressure afforded by the pump is nearly an atmosphere (25 to 27 inches) the ordinary flasks (used for boiling, etc.) are not strong enough, and a bottle, or side-necked flask of the Erlenmeyer shape, constructed of heavier glass, should be used.

The use of *weighed filters* is best avoided if possible, since the filter-paper readily changes in weight under different conditions of the atmosphere. When weighed filters are to be used, they should be placed inside of a tube capable of being tightly stoppered, or between two watch-glasses held together by a clip. Then, after drying in the air-bath, and while still warm, close the tube or watch-glasses, and weigh when cool. Pursue the same method after filtration, so that the paper is weighed as nearly as possible under the same conditions on both occasions. Of

course the smaller the paper the less the error from that source. A weighed filter in a Gooch crucible is the most satisfactory.

Counterbalanced filters are used by some, but the risk of error is greater with them than in the case of weighed filters. Two papers are selected, as nearly as possible of the same size, weight, and texture, and these are counterpoised on the balance, one or the other being trimmed with the scissors until they counterpoise exactly. Then both are folded and placed in the funnel, the inner one receiving the precipitate, the outer one serving as a counterpoise. The theory is, that being subjected to precisely the same treatment, the papers will always exactly counterbalance each other—an assumption open to much question.

In washing, allow all the solution to run through the filter before adding any water, then fill up the filter with water, and allow that to run through before adding more. By this means excessive quantities of wash-water may be avoided. In washing by decantation, which is necessary with some precipitates, the same principle is used. Allow the precipitate to settle, decant as closely as possible, pouring the liquid through the filter, add water, stir well, let settle, and decant again closely before adding more wash-water.

The solutions tend to rise to the top of the paper by capillary action, and to evaporate from there, so that unless care is taken to *wash from the top down*, a ring of soluble salts may remain at the upper edge of the paper, after the precipitate and point of the filter have been well washed out.

Crucibles and Ignition.—Crucibles should always have covers, and be cooled and weighed with them on, to avoid loss of substance and to exclude dust, etc.

Platinum crucibles which heat up and cool down quickly are to be preferred. For the ignition and weighing of most precipitates a small platinum crucible (20 gms.) may be

used, or a shallow platinum dish, for which a piece of platinum-foil may be used as a cover. The latter is advantageous, since the oxidation and destruction of the filter is more readily effected in it. Expense may be saved by the use of porcelain crucibles for this purpose, though these are not quite so convenient.

Previous to ignition the filters and contents must be thoroughly dried; this may be done in the weighed crucible or dish, by exercising proper care. On ignition the paper must be thoroughly consumed, so that no carbon remains. Heat gently at first, with the crucible or dish covered so as to carbonize the filter *without flame*, afterward intensely. The destruction of the filter-paper is most readily effected by tilting the crucible, with the cover partly off, and so inclined as to turn a gentle current of air into the crucible. The flame of the burner should never be allowed to play into the crucible, the object being the exposure of the highly heated (ignited) carbon to the oxidizing influence of the air.

If the last portions of carbon burn off with difficulty, it may be well to remove the flame for a few minutes, and thus allow the air to be drawn into the interstices. Then on applying the flame again, much of the carbon (possibly all) will burn off. Sometimes it may be necessary to *cool* the crucible or dish, and then to stir the contents with a stout platinum wire or a glass rod (which has been *previously heated* in the flame of the burner) in order to expose a fresh surface to the oxidizing influence; then apply the flame as before.

A method applicable to all (ignitable) precipitates, but of especial service in the case of magnesium-ammonium phosphate, is as follows: Dry the precipitate and filter in the funnel, then transfer the precipitate so far as possible to the (weighed) crucible or dish, sweeping off the last portions by means of a feather.* During this operation the

* A small camel's-hair brush is much less satisfactory for this purpose than a feather trimmed to convenient shape.

crucible or dish should stand on a piece of clean glazed paper (preferably black). Then roll up the filter, and taking a 6 or 8 inch length of slender platinum wire, wrap one end of it about the paper to form a sort of cage. Now, holding the other end of the wire so that the filter is above the crucible, apply the flame of a Bunsen burner to the paper until it is burned to ash and drops into the crucible. Then by means of the feather sweep into the crucible any particles of precipitate or filter-ash that may have fallen on the glazed paper. Then place the crucible on a triangle, and apply the heat, gradually at first, finally increasing it to the highest heat obtainable from the burner. If the substance is one which may be reduced by the carbon of the filter-paper (as lead sulphate, etc.), moisten with a little concentrated nitric acid or strong solution of ammonium nitrate before igniting. Where the most of the precipitate can be removed from the filter without loss, it is better to do so, and reserve the precipitate in a watch-glass or convex cover until the filter-paper has been consumed.

Where substances readily reducible are to be weighed, which might form a fusible alloy with platinum (lead sulphate, silver chloride, etc.), porcelain crucibles should be used.

Care of Platinum Ware.—Platinum crucibles, dishes, triangles, etc., after having been exposed to high heats, should be scoured with sea-sand (round grains) after each heating, especially when new. This hardens the surface and often prevents cracking, and the articles last much longer. Heating platinum ware in contact with metallic iron or nickel will produce stains which are removed with difficulty. Gray blotches, which may occur from the contact of gas-flames when the combustion is incomplete, should be removed by scouring with sea-sand.

If the inside of the vessels become stained, they may sometimes be cleaned by introducing concentrated hydrochloric acid, and heating for some time on the water-bath.

If that fails, fuse alkaline carbonates in them, and then treat with strong hydrochloric acid. A repetition of this treatment may be necessary in obstinate cases. Cleansing by fusing potassium bisulphate in the vessels is recommended by some, but seems to be less advantageous than the proceeding mentioned.

Platinum softens decidedly when heated to a full yellow heat; hence triangles should be well secured to the ring of the stand beforehand, especially when a heavy crucible with a full charge is to be supported at a high heat for some time.

The following substances should not be heated (to redness or higher) in platinum:

Free Metals.—Some as iron, nickel, etc., stain the platinum with oxide; others, more readily fusible, as lead, silver, tin, etc., alloy with the platinum and “cut out” the vessel almost immediately.

Oxides or Salts of Fusible Metals in contact with *Reducing Agents*, as carbonaceous substances (filter-paper), sulphides, etc.—The effect is the reduction of the metal, producing essentially the results mentioned in the preceding paragraph.

Caustic Alkalies and Alkaline Earths, which at the fusion or ignition temperature attack the platinum.—Alkaline or alkaline earth nitrates on ignition afford oxides which attack the platinum in the same manner. When the use of alkaline nitrate in a fusion is indispensable, the fusion should be maintained for but a short time (two or three minutes), or the amount of nitrate should be limited so far as possible, and it should be largely diluted by the use of fluxes having practically no action on the platinum (as alkaline carbonates).

Borax slowly decomposes when kept in fusion for some time, and consequently attacks platinum if kept fused in contact with it for a long time. Mixed with alkaline carbonates the attack is much diminished, though not absolutely prevented.

Organic substances containing phosphates (as bread, flour, etc.) when ignited in platinum render the metal temporarily brittle.

Solutions of salts or mixtures which may yield chlorine by concentration (Fe_2Cl_6 , MgCl_2 , etc.; acid mixtures of chlorides and chromates, etc.) should not be evaporated in platinum.

Caution must also be exercised in the ignition of precipitates containing platinum (K_2PtCl_6 , etc.). In these the metal is usually left in a very finely divided condition, and if the heat is too high, it may fuse to the dish or crucible, leaving a permanent roughness.

The softening of platinum at high heats suggests that it may be welded; and such is the fact. In the case of the breaking of a wire, as a triangle, the ends may be interlocked, heated in the flame of a blast-lamp, and then welded together with a hammer. In case of a crack, etc., in a crucible, the vessel may be set on a form of plaster, a strip of thin platinum foil applied at the break, and then heated by the blast, when it can be welded to its place with a smooth-headed hammer. In the latter case, however, some find it more convenient to solder with gold.

Note-Books.—Notes should never be kept on loose scraps of paper, but in regular note-books, of a size sufficient to allow of keeping a clear record of the work, for reference at any time. It is convenient to get in the habit of setting down the weight of the vessel in which a substance is to be weighed, in the lower line of the two intended for that purpose. In the case given below, the glass for the iron wire and the crucible for the precipitate are always weighed first, but the weight is entered on the lower line of the two, for convenience in subtracting.

As an illustration of a clear and convenient form of keeping a note-book, an example is given. The analysis is supposed to be the determination of iron in iron wire:

Wt. glass + Fe wire.....	6.0765
" "	5.3000
Fe wire taken.....	0.7765
Wt. Crucible + ignited ppt., etc.....	25.5170
" "	24.4059
" ppt. + ash.....	1.1131
" filter-ash.....	0.0031
" ignited ppt.....	1.1090

Calculation :

$$1.1090 \times \frac{112}{160} = 0.7763 \text{ Fe}$$

$$0.7763 \times \frac{100}{0.7765} = 99.97 \text{ per cent Fe.}$$

MAKING UP REAGENTS.

In making up reagents, pure materials and distilled water should be used. In the table below, where salts are mentioned, the crystallized salts (containing water of crystallization) are meant. Salts obtained from dealers, and labelled "chemically pure," are seldom absolutely so, and often afford a sediment when their solutions are allowed to stand. Alkaline solutions, solutions of hydrodisodic phosphate, and of many other reagents on long standing in reagent-bottles frequently react upon the glass to a sufficient extent to become contaminated with silica or other constituents of the glass. The composition of the glass is of course the chief factor in this question, and of late the manufacturers of reagent-bottles have been experimenting with a view to the production of a glass with which such action may be reduced to a minimum. Of manufacturing impurities in reagents, the presence of sulphates in hydrodisodic phosphate, ammonium oxalate, and in sodium acetate is especially to be noted. Sulphates may also occur in sodium or other alkaline carbonates, sometimes as a

manufacturing impurity, sometimes because introduced by heating over a gas-flame.

Tests should always be made for such impurities as may interfere with the work. In some cases the amount of impurity may have to be determined, and an allowance made for it in the work.

<i>Reagent.</i>	<i>Proportions to be used.</i>	<i>1 c. c. of solutions will precipitate :</i>
Barium Chloride	1 gm. salt 10 c. c. water	0.0327 gm. SO_4
*Hydrodisodic Phosphate.....	" " " 10 c. c. "	0.0112 " MgO
*Ammonium Oxalate.....	" " " 24 c. c. "	0.0145 " CaO
Argentie Nitrate..	" " " 20 c. c. "	0.0104 " Cl
†Sulphuric Acid.	1 gm. conc. (gr. 1.84) 5 c. c. water	0.2522 " Ba
" "	1 c. c. " " 5 c. c. "	0.4291 " Ba
Platinic Chloride.	{ 1 gm. metal dissolved in aqua regia, evaporated to dryness and dissolved in 1 c. c. HCl + 9 c. c. water.	0.0890 " K
		0.0480 " K_2O
		0.0750 " KCl
Magnesium mixture, vid. <i>Fres. Quant.</i> § 62, p. 89.	1 gm. MgSO_4 (salt), 1 gm. NH_4Cl (salt), 4 c. c. ammonia, 8 c. c. water.	0.0240 " P_2O_5
Magnesium mixture. † (Gooch, Am. Chem. Jour. i. 412.)	{ 3 gms. MgCl_2 , 8 gms. NH_4Cl , 48 c. c. ammonia, excess boiled out.	(approximately)
		0.020 " P_2O_5
		0.009 " P
Molybdate solution, vid. <i>Fres. Qual.</i> § 55, p. 72.	{ 1 gm. MoO_3 dissolved in 4 c. c. ammonia, poured into 15 c. c. HNO_3 (gr. 1.2).	0.0018 " P_2O_5
		0.0055 " P
Molybdate solution. (Drown, Trans. Am. Inst. Min. Eng. xviii. 94, footnote.)	{ 1 gm. MoO_3 , 4 c. c. ammonia (gr. 0.96), 10 c. c. HNO_3 (gr. 1.2).	(approximately)
		0.0017 " P_2O_5
		0.0007 " P

* Saturated solutions.

† Various degrees of dilution in different operations are required. 1:9 (by volume), as specified, is the most convenient for general use as "diluted sulphuric acid." 1:8 (by volume) is often required. In diluting always pour the concentrated acid into the water contained in a thin glass beaker or flask which will not be broken by the rise of temperature. Cool before using.

‡ At present usually preferred.

Ammonium Carbonate, 1 gm. salt, 1 c. c. ammonia.
4 c. c. water.

* Sodium Carbonate, 2.7 gm. salt, 5 c. c. water.

Ammonia.—The best strength for use has sp. gr. 0.96 containing 10 per cent NH_3 . The strongest form has sp. gr. 0.88, and contains 30 per cent or over. For use this should be diluted with two volumes of water. More frequently dealers supply ammonia of sp. gr. 0.935 to 0.94, containing 20 to 25 per cent NH_3 . This should be diluted with an equal volume of water (1:1). Keep in as cool a place as possible.

Hydrochloric Acid.—Usually supplied of sp. gr. 1.2 (40 per cent HCl). For much of the work it may be diluted with an equal volume of water (1:1).

Nitric Acid.—Usually supplied of sp. gr. 1.40 to 1.42 (70 to 75 per cent HNO_3). Except in special cases, one should use this acid diluted with an equal volume of water (1:1) (sp. gr. approximately 1.2) when "concentrated nitric acid" is specified. And for "dilute nitric acid" the "1.40" acid diluted with three volumes of water (1:3). In any case keep the acid protected from the light, which decomposes it, affording lower nitrogen oxides. The rapidity of the change is proportional chiefly to the intensity of the light, though to some extent the more concentrated the acid the more rapid the decomposition.

* Saturated solutions. As sodium carbonate solution acts strongly on glass by standing, some analysts prefer to make the solution only as it is required for use.

CHAPTER I.

BARIUM CHLORIDE.



The composition of crystallized barium chloride is:

Ba.....	58.147 per cent.
Cl.....	29.099 " "
H ₂ O.....	14.754 " "
	<hr/>
	100.000

Pulverize 8 or 10 gms., and keep the powder in a corked tube or bottle. For the determination of the barium, dissolve 1 gm. in 100 c. c. warm water, containing a few drops of hydrochloric acid. Heat to boiling, and add 2 c. c. dilute sulphuric acid, prepared by adding 1 part by volume of strong acid to 5 parts by volume of water. The precipitate settles best if both solutions are boiling when mixed. After mixing, boil for a short time, and then remove the heat.

To determine whether or not a sufficient quantity of sulphuric acid has been added, place 2 or 3 drops of the clear supernatant fluid on a watch-glass, and add a drop of barium chloride solution. If, upon the addition of the barium chloride, the fluid becomes turbid, with a precipitate of barium sulphate, there is evidently a sufficient quantity of sulphuric acid present to precipitate all the barium in the solution. Should no turbidity appear after adding the barium chloride to the solution on the watch-glass, add 1 c. c. more of the dilute sulphuric acid to the main solution, boil, and test a few drops of the clear fluid, as before. Repeat the testing and addition of acid until the fluid evidently contains an excess. When the precipitation is complete, decant the clear fluid on a filter, without disturbing the precipitate, pour 100 c. c. boiling water on the precipitate, stir well with a glass rod, allow

the precipitate to settle, and decant as before. Repeat this washing by decantation several times. Then, transfer the precipitate to the filter, and wash with hot water until the wash-water does not become turbid when either barium chloride or silver nitrate is added to it. After filtering out the barium sulphate and washing by decantation, and before transferring the precipitate to the filter, substitute a clean empty beaker for the one containing the filtrate, in order that an unnecessary amount of re-filtering may be avoided, should the precipitate of barium sulphate run through the filter, which sometimes happens when the filter-paper is very thin. Dry the precipitate on the filter, and when it is dry brush it from the filter into a clock-glass or small dish as completely as possible; burn the filter in a weighed crucible, keeping the crucible covered until the paper is thoroughly charred. After this, remove the cover and continue to heat until the carbon of the paper is completely consumed and only white ash left. Then transfer the precipitate from the clock-glass to the crucible, ignite thoroughly, cool in a desiccator, and weigh. The weight will be that of the crucible, filter-ash, and precipitate of barium sulphate. Deduct the known weight of the crucible and filter-ash, and from the remainder, which will be the weight of the barium sulphate, calculate the per cent of barium.

The combustion of the filter can be hastened by pressing it against the side of the crucible, while burning, with a clean glass rod.

If the barium sulphate be not completely removed from the filter before burning it, a little may possibly be reduced to barium sulphide by the carbon of the filter. This danger may be avoided by moistening the filter-ash with two or three drops of sulphuric acid, drying, and igniting again, before weighing the precipitate in the crucible.

For the determination of the chlorine, dissolve 0.500 gm. of the pulverized barium chloride in a small conical part-

ing-flask, or matrass, such as is used in the assay of gold. Fill the flask about half full with warm water—warm to about 60° C., and add 16 c. c. of a solution of silver nitrate, prepared by dissolving 1 part by weight of pure silver nitrate in 20 parts of water, add 1 c. c. of nitric acid, cork the flask, and shake well. When the precipitate has settled, add 1 c. c. more of the solution of silver nitrate, and notice carefully whether or not it causes another precipitate. If it should do so, shake, and allow the silver chloride to settle, add another c. c. of the silver nitrate solution, and proceed in the same way until no new precipitate forms, and the solution “brightens,” as it is termed; that is, looks perfectly clear. Heat to 60° C. Allow the precipitate to settle completely, fill the flask with warm water, place over the mouth a weighed porcelain crucible of a proper size to allow the mouth of the flask to touch the bottom of it, and invert it quickly. Hang the flask by means of a wire triangle in a ring of an ordinary ring-stand, over an evaporating dish sufficiently large to hold more than the contents of the flask. Lower the ring until the crucible stands on the bottom of the dish, the crucible being all the time pressed firmly against the mouth of the flask. Fill the crucible with water and gently raise the ring, adding water while doing so, until the mouth of the flask is so slightly submerged that a watch-glass, a trifle larger than the crucible, can be slipped under it. Do not place the watch-glass under the mouth of the flask at first, but allow the whole to stand for some hours, protected as far as possible from the light.

The precipitate will usually settle entirely from the flask into the crucible; should any particles adhere to the sides of the flask, slight tapping will cause them to descend. After all the precipitate has settled into the crucible, slip the watch-glass under the mouth of the flask, and, while holding it firmly against it with one hand, remove the crucible containing the silver chloride with the other; allow the fluid in the flask to run out slowly

into the dish by moving the watch-glass gently with a rocking motion. Now pour the fluid in the crucible carefully into another vessel, or, for greater security, on a filter. Wash repeatedly with hot water, containing a little nitric acid, decanting on the filter as before, until the washings do not become turbid upon the addition of hydrochloric acid. In testing, use only a few drops at a time, in a very slender test-tube. Remove the last drops of fluid from the crucible with a strip of bibulous paper, being careful not to take up any silver chloride; should any particles adhere, they can be washed back into the crucible, and the fluid removed as before. By a little care and dexterity, all but a very small quantity of fluid can, in this way, be removed. Evaporate off what remains in the crucible, and then dry it, with its contents, in a drying chamber. When all visible moisture is removed, heat over a low flame, until the silver chloride begins to fuse well around the edge; cool and weigh. Deduct from this weight the known weight of the crucible. The remainder will be the weight of the silver chloride. From this, calculate the per cent of chlorine. The silver chloride should not be fused at a high heat, as it will volatilize some of it. This is the best method of determining chlorine gravimetrically, where a large quantity of silver chloride is to be handled.

The silver chloride can be precipitated in a beaker instead of a flask, and filtered out. Precipitate in the same way as directed above; pour the clear fluid on the filter, wash a few times by decantation with hot water acidulated with nitric acid, transfer the precipitate to the filter, and wash with hot water acidulated with nitric acid, until the washings do not become turbid upon the addition of hydrochloric acid, to be sure that the excess of silver nitrate is washed out. Dry the precipitate in the funnel in an air-bath. When the precipitate is dry, transfer it to a clock-glass, brushing the filter as clean as possible with a feather; place the filter in a weighed porcelain crucible, moisten it with a few drops of nitric acid, and burn it

until all carbon is consumed. Let the crucible cool enough to be handled, add a few drops of nitric acid, and warm, to dissolve the metallic silver which is due to the reduction of the silver chloride by the carbon of the filter. Then add a few drops of hydrochloric acid and evaporate to dryness. Transfer the precipitate from the clock-glass to the crucible, fuse as directed above, cool and weigh. The weight will be that of the crucible, filter-ash and silver chloride. Deduct the known weight of the crucible and ash of filter; the remainder will be the weight of the silver chloride. From this, calculate the per cent of chlorine.

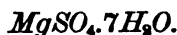
Whichever method be employed, evaporate the filtrates and washings to small bulk, after adding a little silver nitrate and nitric acid. Should a precipitate of silver chloride be formed, treat it as directed above, and add the per cent to the first.

For the determination of water, introduce 1 gm. into a weighed crucible, and heat very gently to low redness; cool and weigh. Repeat the heating and weighing until the substance ceases to diminish in weight. Care should be taken not to heat too highly, as by doing so some chlorine may be expelled.

The loss of weight is equivalent to the water; from this, calculate the per cent of water.

CHAPTER II.

MAGNESIUM SULPHATE.



The theoretical composition of magnesium sulphate is :

MgO.....	16.26	per cent.
SO ₃	82.52	" "
H ₂ O.....	51.22	" "
	<hr/>	
	100.00	

As the salt is slightly efflorescent, select 8 or 10 gms. of crystals that have not lost water by exposure, pulverize them quickly, and keep the powder in a corked tube or bottle.

For the determination of magnesia, dissolve about 1 gm. in 25 c. c. of cold water in a small beaker, add enough hydrochloric acid to make the solution distinctly acid to test-paper, and then enough ammonia to make it decidedly alkaline. Should a precipitate of magnesium hydrate occur, make the solution acid again with hydrochloric acid, and then alkaline again with ammonia, as before. Repeat this treatment if necessary until ammonia no longer produces a precipitate. Allow the fluid to cool, and add 16 c. c. of a solution of hydro-disodium phosphate, prepared by dissolving 1 part by weight of the salt in 10 parts of water. Agitate the contents of the beaker well with a glass rod, being careful not to rub the sides of the vessel with the rod, as it will cause crystals of ammonia-magnesium phosphate to adhere to the glass so tenaciously as to be difficult to remove. Allow the solution to stand cold 12 hours, and, when the precipitate has entirely settled, place 3 or 4 drops of the clear fluid on a watch-glass, or in a very small test-tube, and add 2 or 3 drops of "magnesia mixture." If a precipitate forms, it shows that enough hydro-disodium phosphate has been used ; if no precipitate forms, add 5 c. c. of the precipitant to the main solution, and proceed as before. Filter on a very

small filter, and wash with dilute ammonia, prepared by mixing 1 part of strong ammonia with 2 parts of water, until no turbidity is produced by silver nitrate in 1 c. c. of the washings acidulated with nitric acid, or by barium chloride in the same quantity acidulated with hydrochloric acid. Dry the precipitate on the filter, and, when it is dry, brush it from the filter into a large watch-glass, and burn the filter in a weighed crucible. When the carbon of the filter is entirely consumed, transfer the precipitate to the crucible, and ignite again, increasing the heat to bright redness, keeping the crucible covered. Then remove the cover, and heat strongly, until the contents of the crucible are white, or nearly so. Should the contents of the crucible appear dark in color, moisten them with a few drops of nitric acid; evaporate off the excess of acid carefully, and ignite again, until the precipitate is of a light gray color. Cool the crucible and contents in a desiccator, and weigh. Deduct the known weights of the crucible and filter-ash. The remainder will be the weight of the magnesium pyro-phosphate ($\text{Mg}_2\text{P}_2\text{O}_7$). From this weight calculate the per cent of magnesia.

For the determination of the SO_3 , dissolve 1 gm. in 100 c. c. warm water, acidulate slightly with hydrochloric acid, boil, add 12 c. c. of a solution of barium chloride—prepared by dissolving 1 part by weight of crystallized barium chloride in 10 parts of water—and continue the boiling for 2 or 3 minutes. Allow the precipitate to settle, and test a few drops of the clear fluid with sulphuric acid. If no precipitate is produced by the sulphuric acid, there cannot be an excess of barium chloride in the solution. In such a case, add another c. c. of barium chloride solution, stir, and allow the precipitate to settle, and test again. Proceed in the same way, until the appearance of a precipitate upon testing shows that there is a sufficient quantity of barium chloride present. Finally, allow the precipitate to settle, decant the clear fluid on a filter, pour on the precipitate 100 c. c. of boiling water containing 2 or 3

drops of hydrochloric acid, stir, allow the precipitate to settle, and again decant on the filter. Repeat this treatment, and then transfer the precipitate to the filter with hot water, and wash with the same until a few drops of the wash-water show no turbidity when treated with silver nitrate, and leave no more residue, when evaporated on platinum and ignited, than will be left by a similar quantity of distilled water, treated in the same way. Dry the precipitate, brush it on a clock-glass, burn the filter moistened with a few drops of sulphuric acid in a weighed crucible, add the precipitate, ignite strongly, cool, and weigh. Deduct the known weights of the crucible and filter-ash. The remainder will be the weight of the barium sulphate. From this calculate the per cent of SO_3 .

As the precipitate of barium sulphate has a tendency to carry down with it barium chloride, which it is difficult to remove by washing, after igniting the precipitate, brush it from the crucible into a beaker, moisten with a few drops of hydrochloric acid, add water, and boil. Then transfer all to a filter, wash well, dry, ignite, and weigh. Where barium sulphate has been precipitated in a fluid containing salts of iron, it is nearly impossible to purify it in this manner. In such a case, fuse the ignited precipitate with a little sodium carbonate, digest the mass with boiling water until it is disintegrated, transfer it to a filter, and wash well. By this means, the barium will remain on the filter as carbonate, with the impurity, while the sulphuric acid will pass into the filtrate, from which it can be precipitated free from impurity.

For the determination of the water, introduce about 1 gm. of the salt into a weighed crucible, heat to redness, cool, and weigh. Again heat, cool, and weigh. Repeat until the crucible and contents no longer lose weight by being heated. The difference between the weights of the crucible and contents, before and after heating, is due to the loss of water. From this, calculate the per cent of water.

CHAPTER III.

CALCIUM CARBONATE.



The theoretical composition of calcite is :

CaO.....	56.00	per cent.
CO ₂	44.00	“ “
	<hr/>	
	100.00	

For the determination of the lime, dissolve 1 gm. in 3 c. c. of strong hydrochloric acid, and 25 c. c. of boiling water. It should dissolve completely; should it not, filter out any residue, and wash with about 50 c. c. of hot water. Then wash the residue from the filter into a very small beaker with as little water as possible, and add 2 c. c. of hydrochloric acid, and boil. Should it dissolve, add the solution to the first one; should it not dissolve, pass the fluid through the same filter, wash, and add the filtrate to the first solution. The combined solutions should not amount to more than 200 c. c. Dry the insoluble residue, burn it in a weighed crucible, and deduct its weight from the original weight of substance. The difference expresses the actual weight of calcite taken for analysis. To the combined solutions add enough ammonia to make the fluid faintly alkaline to test-paper, heat to boiling, and add 50 c. c. of ammonium oxalate solution, prepared by dissolving 1 part by weight of the salt in 24 parts of water. Boil hard for two or three minutes. Then remove the heat, allow the fluid to cool and the precipitate to settle. To be sure that enough ammonium oxalate has been used, put 3 or 4 drops of the clear fluid on a watch-glass or in a small test-tube, add 1 drop of ammonia and two or three drops of solution of calcium chloride. The formation of a precipitate proves that enough ammonium oxalate was used in the first instance. If no precipitate

forms, add 10 c. c. more ammonium oxalate to the main solution, and test again in the same way. Proceed in this manner until assured that enough of the precipitant has been added. When the precipitate has thoroughly settled, decant the clear fluid on a filter, after pouring off as much of the fluid as possible. Without disturbing the precipitate, remove the beaker containing the filtrate, and place another under the funnel. Then transfer the precipitate to the filter with hot water, and wash it down into the point. More washing than will effect that object is unnecessary, as the impurities that may possibly be present, that is, ammonium chloride and oxalate will be expelled by the after-treatment of the calcium oxalate with sulphuric acid. The object aimed at in removing the beaker containing the filtrate is to avoid having to re-filter a large amount of fluid, should the precipitate of calcium oxalate run through the filter, as it sometimes does, particularly when the filter-paper is very thin. Remove any calcium oxalate adhering to the walls of the beaker with a feather or rubber. If any adhere so tenaciously as to render it impossible to remove it with a rubber, wash it off with a little dilute hydrochloric acid into a small beaker; add ammonia to alkaline reaction, a few drops of ammonium oxalate, and boil two or three minutes. When the precipitate has settled, filter through the same filter. The water required to transfer the precipitate to the filter will wash it sufficiently. Dry the filter and contents at a temperature not exceeding 100° C., to avoid making the filter brittle. When the precipitate is dry, brush it into a clock-glass, cleaning the filter as thoroughly as possible. Burn the filter in a weighed crucible until only white ash is left. Remove the heat, and when the crucible is cool, transfer the precipitate from the glass to the crucible, add enough strong pure sulphuric acid to moisten the precipitate, place the lid on the crucible and expel the excess of sulphuric acid by heating over a Bunsen burner, allowing the flame to touch only the lip

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A and B, hold
about 25 c. c.



decorated cork, or
the stopper of
ing, about one

and a half inches long. Through the other hole, passes, nearly to the bottom of the flask, one limb of a glass tube bent twice at right angles, the other limb of which passes through the first hole of the stopper of the other 100 c. c. flask, *B*, nearly to the bottom. Through the other hole of the stopper of flask *B*, sufficiently far to clear the stopper, passes the short limb of a tube, bent twice at right angles, while the longer limb passes through the first hole of the stopper of the 25 c. c. flask, *C*, nearly to the bottom. Through the other hole, passes a short tube, about one and a half inches long. Into flask *A*, introduce 30 c. c. of dilute nitric acid; into flask *B*, a carefully-weighed quantity of the calcium carbonate (about 1 gm.), and into flask *C*, 10 c. c. of concentrated sulphuric acid. Put the apparatus together, and weigh. Then draw a little acid over from *A* into *B*, by sucking at the exit tube of *C*, and close the open tube of *A* by placing over it a short piece of rubber tubing, the other end of which is closed by a piece of glass rod. When the violent effervescence is over, open the closed tube of *A*, and repeat the operation, until enough acid is drawn from *A* into *B* to decompose the calcium carbonate. Then close the open tube of *A*, and raise the contents of the flask *B*, to incipient boiling. Then remove the heat; at the same time, remove the stopper from the open tube of *A*, attach in its place a small calcium-chloride tube, containing equal parts of calcium chloride and soda lime, and draw a gentle current of air through the apparatus by means of an aspirator. The air should not pass more rapidly than at the rate of 2 bubbles in a second, or the aspiration be continued longer than is necessary to clear the apparatus of carbonic acid. The passage of half a litre of air will effect this. The amount can be determined by the volume of water that escapes from the aspirator. The carbonic acid can be sucked out by the mouth. If this plan be adopted, the air should be drawn through until it no longer tastes of carbonic acid. After a sufficient volume of air has been drawn through the

apparatus to extract the carbonic acid, allow the apparatus to cool, remove the aspirator, if one has been used, and the calcium-chloride tube from the open tube of flask *A*, and weigh. The difference between this and the first weight of the apparatus is equivalent to the weight of carbonic acid. In many cases, the determination of carbonic acid by loss is inadmissible. In such cases, it is absorbed in some substance with which it will combine, as potassium hydrate or soda-lime. For this purpose, an apparatus such as that described by Fresenius in his work on Quantitative Analysis (§ 139 e p. 293), under the head of carbonic acid, can be used. In making the determination, do not use more than 0.500 gm. of calcium carbonate, as a large quantity necessitates the use of large absorption tubes. If soda-lime be used, it is well not to use the tube after more than one half of the contents have been heated by the carbonic acid.

For the analysis, weigh the absorption tubes, introduce the weighed substance into the decomposing flask, put the apparatus together, close the stop-cock of the funnel-tube, and attach the aspirator. After the aspirator has drawn long enough to produce a partial vacuum in the apparatus, introduce about 30 c. c. of dilute nitric acid, through the funnel-tube, into the decomposing-flask. As soon as all the acid is in, close the funnel-tube. After the first violent effervescence has ceased, apply gentle heat to the flask, and gradually increase it, until the fluid in the flask begins to boil. Then remove the heat, attach the guard tube, containing soda lime and calcium chloride, open the stop-cock or clamp, and draw air through the apparatus, very slowly, until the absorption tubes are cool, or until about 2 litres of air have passed through. When the tubes are cool, weigh them. The difference between this weight and the first weight of the tubes is equivalent to the carbonic acid. The carbonic acid can also be determined by introducing a weighed quantity into a tube of hard glass, by means of a small platinum

ATE.

At the same time, drawing dried air. Attach to the neutral calcium chloride, and passed for some time. Allow the carbonic acid to be expelled from the sub- contents, and also the weight of the boat while the increase of weight will be water. The weight of carbonic acid and water, the weight of water will be that of 0.500 gm. of substance

The weight of the carbonic acid is repre-



with a cork. *b* is provided with sulphuric acid. *c* contains sulphuric acid. *e* contains pumice which has been heated with soda-lime and *h* sulphuric acid on a water-bath. The apparatus should be previously heated with water to drive off any gas liable to contain chlorides and the temperature should not rise above the bend.

The weights are weighed. They should be weighed in a glass rod to prevent absorption of

absorption bulbs of
are charged with a



Geissler Bulbs.

escape. Some find it
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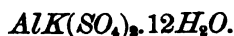
Some may be de-
composed of oxalic acid
precipitated as oxalate.
It is prepared in the manner
with hot water to
be dissolved by pour-
ing dilute sulphuric
acid at 60° C. or over, but
it is a standard solution
ordinarily used for
Ammonia Iron
analysis in from a bu-
bbling to the solu-

should contain about
10 c. c. (this being the
volume of the same
solution containing
10 c. c. of $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$)
solution 1 c. c. con-
taining 10 c. c. to combine with
the lactic-acid solution
three or four lots
more of diluted

sulphuric acid, and heating. The standardization is conducted essentially in the same manner as the titration. The equations are practically; with oxalic acid: $K_2Mn_2O_8 + 5(H_2C_2O_4 \cdot 2H_2O) + 3H_2SO_4 = 10CO_2 + K_2SO_4 + 2MnSO_4 + 18H_2O$. With calcium oxalate: $K_2Mn_2O_8 + 5CaC_2O_4 + 8H_2SO_4 = 10CO_2 + K_2SO_4 + 2MnSO_4 + 5CaSO_4 + 8H_2O$. A decided excess of sulphuric acid is always necessary. It may be noted that the value of the permanganate solution in CaO is exactly half its value in metallic iron (cf. Chapter IX.). The volumetric method for lime is more conveniently applied where the percentage of lime is low. 0.4 to 0.5 gm. of pure $CaCO_3$ will afford calcium oxalate requiring nearly if not quite 100 c. c. of the above-mentioned permanganate solution.

CHAPTER IV.

POTASSIUM ALUM.



The theoretical composition of potassium alum is :

Al ₂ O ₃	10.86	per cent.
K ₂ O.....	9.90	" "
SO ₃	88.72	" "
H ₂ O.....	45.52	" "
	<hr/>	
	100.00	

Pulverize 5 or 6 gms. coarsely and quickly, and keep the powder in a small corked bottle, or specimen tube. For the determination of alumina, first weigh the tube, and contents; then shake out a little into a beaker, and again weigh the tube, and remaining substance. The diminution in weight, of course, shows the amount taken. Proceed in this way until about 1 gm. has been transferred to the beaker. Pour upon it 100 c. c. of hot water and stir; when all is dissolved, add 2 or 3 c. c. of strong hydrochloric acid, and enough ammonia to turn red test-paper blue, and emit a slight odor of ammonia. Be cautious not to add a large excess, or time will be wasted in boiling it out, which will be necessary for the reason that aluminum hydrate is somewhat soluble in excess of ammonia. Boil until the vapors no longer smell of ammonia, and do not turn turmeric paper brown. Allow the precipitate to settle, and decant the clear fluid on a filter. Then pour 40 or 50 c. c. of boiling water on the precipitate, stir, allow it to settle, and decant the clear fluid on the filter as before. Repeat this treatment several times, and finally transfer the precipitate to the filter, with boiling water, and wash with the same, until a few drops of the wash-water, acidulated with nitric acid, do not show a precipitate of silver chloride when treated with

a drop of silver nitrate, or a precipitate of barium sulphate when treated with hydrochloric acid and barium chloride. It is unnecessary to begin washing on the filter until about 100 c. c. have passed through the filter. Test the filtrate and washings with litmus paper. If they are not alkaline, add ammonia until the fluid is faintly alkaline, and heat. Should a precipitate appear, filter it out, wash, dry it, and reserve it to be burned with the other. When the main precipitate is perfectly dry, ignite it, with the smaller one, should there be any, rolled up in the filter, in a weighed crucible furnished with a lid, applying the heat gently at first, and then intensely, in order to expel any adhering sulphuric acid. During the latter part of the ignition remove the cover from the crucible, in order thoroughly to consume the filter. When the filter is completely burned, remove the heat, cool and weigh. This weight, after deducting the weight of the crucible and filter-ash, will be the weight of the alumina.

For the determination of SO_3 concentrate the filtrate from the alumina to 200 c. c. by evaporation, add hydrochloric acid until the fluid is slightly acid, and then add 12 c. c. of barium chloride solution, prepared by dissolving 1 part by weight of crystallized barium chloride in 10 parts of water. Boil for a few minutes and allow the precipitate of barium sulphate to settle, and proceed as directed in the analysis of magnesium sulphate. Observe the precautions there given, as to washing and purification of the precipitate.

To determine the potassium, add ammonia to the filtrate from the barium sulphate until it is slightly alkaline, warm slightly, and add ammonium carbonate as long as it produces a precipitate of barium carbonate. Let stand cold to settle, decant the clear fluid on a filter, and wash by decantation 3 or 4 times in the cold, using a few drops of ammonium carbonate each time. Transfer to the filter, and wash with diluted ammonium carbonate until 2 or 3 drops of the wash-water, acidified with nitric acid, show

no cloudiness when treated with silver nitrate. Pour 3 or 4 funnellfuls through the filter before beginning to test. When all the potassium chloride is washed out, evaporate the filtrate and washings to dryness in a platinum dish, and ignite to faint redness, until all the ammonium chloride is expelled. This may be ascertained by holding over the vessel a clean cold clock-glass. The non-appearance of a white coating on the glass indicates the absence of ammonium chloride. Dissolve the residue in about 25 c. c. of warm water, filter the solution into a small porcelain dish, and wash with hot water, testing the wash-water with silver nitrate, as directed above, to be sure that all potassium chloride is washed out. When the filter and contents are sufficiently washed, add to the fluid 2 drops of concentrated hydrochloric acid and 8 c. c. of platinum tetrachloride solution, prepared by dissolving 1 part by weight of platinum tetrachloride in 10 parts of water, and evaporate to a pasty consistency, on a water-bath. Then pour into the dish about 50 c. c. of alcohol, of about 90 per cent, without removing the dish from the bath, and heat for two or three minutes. Now rinse the contents of the dish into a small flask, marked A, with alcohol of 90 per cent, and cork it immediately, to avoid the possibility of absorption of ammonia from the air of the laboratory, of which there is frequently great danger. After the potassium platino-chloride has entirely settled, and the fluid shows by its color that a sufficient amount of platinum tetrachloride has been added, pour off the clear fluid upon a filter, protecting the solution from absorption of ammonia fumes. When all of the solution has been decanted onto the filter, transfer the precipitate to a small beaker thus: run about 20 c. c. of cold alcohol into the flask, then cover the mouth of the flask with the side of the left hand, while the flask is supported by the right. Holding the flask thus, invert it, and give the contents a whirling motion so as to bring all of the precipitate down against the left hand. Hold the mouth of the flask close down over

the (clean) beaker, and remove the hand, so that the precipitate with the fluid all falls into the beaker. Rinse off the precipitate which may adhere to the hand with a stream from the alcohol wash-bottle; repeat this, if necessary. The transfer of the precipitate to the filter is much more readily effected from the beaker than from the flask. The filtrate and washings which are decidedly colored with the platinum salt should be evaporated to small bulk, and then taken up with alcohol to recover any precipitate that may be capable of forming. Dry the filter and contents in an air-bath at 100° C. Ignite the dry precipitate, rolled up in the filter, in a weighed crucible, applying the heat very gently at first, and keeping the crucible covered until the filter-paper is charred. Then remove the cover from the crucible, and ignite at a higher degree of heat, until the filter is entirely consumed. Allow the crucible to cool, add a little oxalic acid, heat gently at first, until the water of crystallization of the oxalic acid is expelled, and then more intensely until the acid is decomposed, and all the carbon consumed. Cool the crucible, and wash by decantation with hot water as long as the wash-water becomes turbid from formation of silver chloride, when treated with silver nitrate. By this means, the double chloride is decomposed, and all the potassium and chlorine washed out, leaving only spongy platinum. Heat alone fails to decompose the compound completely.

After the platinum is sufficiently washed, dry the crucible and contents, and ignite until every thing is consumed but spongy platinum. Cool, and weigh. Deduct from this weight, that of the crucible and filter-ash. The remainder will be the weight of platinum. From this, calculate the per cent of potassium or of potassium oxide.

After all the alcohol has been expelled from the original filtrate by evaporation, as directed above, add 1 c. c. of platinum tetrachloride solution, and a very small quantity of pure sodium chloride; continue the evaporation to

pasty consistency, treat with alcohol, and proceed as directed for the treatment of the main precipitate. Should any more potassium platino-chloride be obtained, treat it as above, and add the per cent to that of the main precipitate. The sodium chloride tends to prevent the decomposition of the platinum chloride, while evaporating the alcoholic solution.

The precipitate may also be dried and weighed as K_2PtCl_6 , in which case it had best be filtered through a Gooch crucible containing a filter-paper cut to fit, or better a filter-bed of asbestos (*vid.* Introduction—Filtering, etc.).

The Lindo-Gladding method for determining potash, devised for the analysis of fertilizers (*vid.* Bulletins of U. S. Dept. of Agriculture, Nos. 31, 35, 38, 43, etc., Reports of meetings of Soc. of Off. Agri. Chemists), is applicable in this case as in others (salts present as sulphates, lime and alkaline earths absent, also salts of the heavy metals absent).

Weigh out 1 gm. of the alum in a small evaporating-dish; dissolve in as little hot water as possible (filter clear if necessary), add 3 c. c. of platinic-chloride solution, and evaporate on the water-bath to a pasty consistency. Remove from the heat, and add 50 c. c. of alcohol (of about 90 per cent). Stir well, and then allow to stand for at least two hours in a cool place, inverting a beaker over the dish, or by some other means protecting it from possible access of ammonia fumes. Meantime prepare a Gooch filter containing a filter-bed of (washed) asbestos. Dry and weigh the Gooch filter; then filter the solution through it, transferring the precipitate to the filter by a stream from the alcohol wash-bottle. Wash a few times with alcohol, after the washings run apparently colorless. The precipitate held on the filter should now consist only of K_2PtCl_6 , together with sulphates insoluble in alcohol. To remove the latter, wash with a water solution containing 100 gms. ammonium chloride in 500 c. c. of water, which solution has been shaken (cold) with potassium

platinic chloride until it is saturated. The amount of K_2PtCl_6 which it will dissolve is so small that the solution has only the faintest possible yellow tinge. Use 10 c. c. of this solution for each washing, allowing it to run through slowly, especially at first. Repeat the washing five or six times. Then wash off the adhering ammonium chloride by three or four washings with alcohol; suck dry. Dry in the air-bath and weigh. It may be deemed preferable not to weigh the Gooch filter beforehand, but to dissolve the precipitate through the filter with hot water into a weighed capsule, and to evaporate, dry, and weigh, or to decompose by ignition with oxalic acid as already described, and weigh the platinum. According to the Soc. of Off. Agri. Chemists, the weight of the K_2PtCl_6 multiplied by 0.19308 gives its equivalent in K_2O .

For the determination of water, weigh out about 1 gm., and dry in an air-bath at $250^{\circ}C.$, until it ceases to lose weight. The loss at this temperature is water.

CHAPTER V.

CALCIUM FLUORIDE.



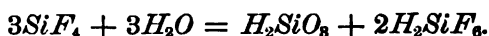
The theoretical composition is :

Ca.....	51.28	per cent.
Fl.....	48.72	" "
	<hr/>	
	100.00	

Introduce into a weighed platinum crucible 1 gm. of the finely-powdered mineral, mix it, by means of a coarse platinum wire, with pure concentrated sulphuric acid, to the consistence of paste ; add enough more acid to make the mixture semi-fluid, place the crucible with the cover on, in an inclined position on a support, and heat with a Bunsen burner, allowing the flame to strike the edge of the crucible and lid. Continue heating until all the sulphuric acid is expelled, and the calcium converted into sulphate, cool, weigh, and calculate the weight of calcium. The difference between the weight of calcium and the weight of mineral taken is equivalent to the weight of fluorine expelled. From these data, calculate the per cent of calcium and fluorine.

There are various methods for determining fluorine, varying in complexity with the character of the substances treated. It was suggested by Berzelius (Rose, p. 883) to distill the fluoride of silicon from substances that could be decomposed by sulphuric acid, by heating with this acid, adding powdered silica if necessary, in a retort of lead or platinum, delivering into a vessel of water. The acid used must be pure and concentrated, the silica pure and in the form of very fine powder, and the metallic tube connected with the retort must dip into mercury just far enough to prevent the point from coming in contact with

the water, or the separated silica will clog it. The fluoride of silicon, when it comes in contact with the water, is decomposed into silica, which separates, and hydro-fluosilicic acid, which goes into solution. Filter out the silica, wash it well, dry, and weigh it. To the acid fluid containing hydro-fluosilicic acid, Rose (*lb.* p. 883) adds potassium chloride and alcohol. The potassium silico-fluoride is collected on a weighed filter, washed with dilute alcohol, consisting of equal parts of alcohol and water, dried at 100° C., and weighed. The fluorine calculated from the silica, and from the precipitate of potassium silico-fluoride, will together give the per cent in the substance.



To determine the fluorine in substances insoluble in water, and not decomposable by acid, Berzelius (*Vid. Fres. Quant.*, § 166a) fused the substance with 4 parts of sodium carbonate at a strong red heat, digested the mass in water, boiled, filtered, and washed, first with boiling water, then with a solution of ammonium carbonate. The filtrate will contain all the fluorine as sodium fluoride, together with carbonate, silicate, and aluminate of sodium. The filtrate is to be mixed with ammonium carbonate, and the mixture heated, the ammonium carbonate which evaporates being replaced. The aluminium hydrate and silicic acid is then filtered off and washed with ammonium carbonate. The filtrate is then heated until the ammonium carbonate is completely expelled, and the fluorine determined. Rose suggests a modification of Berzelius's treatment after reaching this point, which is as follows: Add a solution of calcium chloride as long as a precipitate continues to form. When the precipitate, which consists of calcium fluoride, and calcium carbonate, has subsided, it is washed, first by decantation, afterward on the filter, and dried. When dry, it is ignited in a platinum crucible. Water is then

poured over it, in a platinum or porcelain dish, acetic acid added in slight excess, the mixture evaporated to dryness on a water-bath, and heated on the latter until all odor of acetic acid disappears. The residue, which consists of calcium fluoride and calcium acetate, is heated with water, the calcium fluoride filtered off, washed, dried, ignited, and weighed. If the precipitate of calcium fluoride and calcium carbonate were treated with acetic acid, without previous heating, the washing of the fluoride would be very difficult. From the weight of the calcium fluoride, calculate the per cent of fluorine.

See H. Rose, *Anal. Chem.*, chapter on Fluorine, p. 757.

NOTE.—Modified forms of Berzelius' method for the determination of fluorine have been recommended. The modifications consist in the use of sufficient amounts of finely divided (best "precipitated") silica to allow of the operation being safely conducted in glass, the passage of *dried* air through the heated mixture to facilitate the removal of the silicon fluoride, and finally the titration of the solution of potassium chloride, into which the silicon fluoride has been passed, by acidimetry, to determine the amount of hydrochloric acid set free by the formation of potassium silico-fluoride.

0.25 to 1 gm. of the material is thoroughly mixed with ten times its weight of precipitated silica, and the mixture is placed in a flask having a capacity of about 100 c. c. This flask is stoppered with a cork carrying a thermometer, and connections—on the one side with a flask containing concentrated sulphuric acid, through which dry air can be drawn,—on the other side with, *first*, an empty U tube immersed in cold water to condense any sulphuric acid that may be carried over; *second*, a flask containing a little mercury, below the surface of which the delivery-tube dips, and on the top of that 30 c. c. of a twenty per cent solution of potassium chloride mixed with an equal bulk of alcohol; *third*, a guard-flask, containing water, intended to hold back any hydrochloric acid carried over by the air-current. (U tubes or Peligot bulb tubes may be used instead of the second and third flasks, and the use of mercury in the second flask thus avoided.)

The third flask is connected with an aspirator. When all is ready, about 15 c. c. of pure anhydrous H_2SO_4 is poured upon the mixture of fluoride and silica, the connections made, and a slow current of air drawn through the train. Heat is then applied to the mixture, gradually raising it to about 160°C ., at which it is maintained for two hours, the aspiration being continued throughout. At the end of that time the apparatus is disconnected, the contents of the second and third flasks mentioned (really the fourth and fifth of the train) is rinsed into a beaker, and titrated with standard alkali. (*Vid.* Alkalimetry and Acidimetry).

CHAPTER VI.

POTASSIUM IODIDE.

KI.

The theoretical composition is :

K	23.545 per cent.
I	76.455 " "
	<hr/>
	100.000

To determine the potassium, dissolve 1 gm. of the salt in about 10 c. c. of water, in a small porcelain dish, add 2 or 3 c. c. strong nitric acid, and evaporate to dryness on the water-bath, to expel the iodine. It may be necessary to repeat this operation in order to drive out the last traces of the iodine. Take up with about 20 c. c. of water, add 1 c. c. strong hydrochloric acid, and proceed as directed in the analysis of potassium alum.

To determine the iodine, weigh carefully 0.250 gm. of the salt, transfer it to a parting flask, add warm water, an excess of silver nitrate and nitric acid, and proceed as directed in the analysis of barium chloride, for the determination of chlorine, care being taken to add excess of silver nitrate before adding the nitric acid.

The iodine can also be determined with great accuracy by precipitating it, as palladium iodide, in a solution of the salt, slightly acidified with hydrochloric acid, warming gently and allowing the whole to stand for about 24 hours, to give the precipitate ample time to form and settle. The precipitate is PdI_2 . After washing, ignite and weigh metallic palladium, and calculate iodine.

See Fres., § 145—1—b, and H. Rose, chapter on Iodine, p. 824.

CHAPTER VII.

POTASSIUM BROMIDE.



The theoretical composition of the salt is :

K.....	33.885 per cent.
Br.....	67.165 " "
	<hr/> 100.000

For the determination of the potassium, proceed exactly as in the previous analysis of potassium iodide, or boil with dilute chlorine water until the bromine is expelled, and then proceed.

The bromine is determined as silver bromide, in the same manner as chlorine is determined as silver chloride, in the analysis of barium chloride.

See H. Rose, *Anal. Chem.*, chapter on Bromine, p. 815.

NOTE.—In either the iodide or the bromide the potassium may be determined as sulphate. Dissolve 1 gm. in 10 c. c. of warm water in a weighed platinum dish, add 10 c. c. dilute sulphuric acid, evaporate, heat cautiously to expel the excess of sulphuric acid, and ignite. Then cool, add powdered ammonium carbonate, and ignite again. Cool and weigh K_2SO_4 . The evaporation affords acid potassium sulphate, with free hydriodic or hydrobromic acid, the latter escaping with the aqueous vapor. The ignition unless very prolonged will not completely decompose the acid potassium sulphate. By use of the ammonium carbonate as described, neutral potassium sulphate and some ammonium sulphate are obtained, which latter, together with the excess of ammonium carbonate, are driven off by the second ignition. If the material contains other than potassium salt, the potassium may be determined by the Lindo-Gladding method. (See Potassium Alum.)

CHAPTER VIII.

HYDRO-DISODIUM PHOSPHATE.



The theoretical composition of hydro-disodium phosphate is :

Na ₂ O.....	17.32 per cent.
P ₂ O ₅	19.83 " "
H ₂ O.....	62.85 " "
	<hr/>
	100.00

Select 4 or 5 gms. of the crystals which have lost no water by efflorescence, break them up quickly into a coarse powder, and keep the powder in a small, well-corked bottle or large specimen tube, and weigh the portions required for analysis as directed in the case of potassium alum.

Perhaps a better plan is to dissolve about 5 gms. in 100 c. c. of water, transfer the solution to a 250 c. c. flask, dilute to the holding mark, and mix the fluid well by pouring several times from the flask into a beaker and back. Then draw from the flask with a pipette the quantity required for analysis, and cork the flask to prevent evaporation of the fluid.

For the determination of sodium, dissolve about 1 gm. of the salt in about 50 c. c. of water, or take an equivalent amount from the solution of a large quantity. Then dissolve about 0.600 gm. piano-forte wire in 30 c. c. dilute hydrochloric acid, add 3 c. c. of strong nitric acid, and boil. Then concentrate the solution until nearly all free acid is expelled, dilute with 10 c. c. of water, and add the solution to that of the sodium phosphate. To the combined solutions add ammonia in excess, and heat to boiling. Then remove the heat, and allow the precipitate to settle. When the precipitate has settled thoroughly,

and the supernatant fluid become colorless, filter off the clear fluid, and wash the precipitate three or four times, using 50 or 60 c. c. of hot water each time. Then transfer the precipitate to the filter, and wash again with hot water, until the washings show only a slight opalescence upon addition of silver nitrate and nitric acid. In testing the washings, use only 2 or 3 drops each time. The precipitate will contain all the phosphoric acid, combined with the ferric oxide, and may be rejected. Evaporate the filtrate and washings to dryness on a water-bath. Just before the point of dryness is reached, add dilute hydrochloric acid, little by little, until the fluid is slightly acid to test-paper. By delaying the addition of the acid until nearly all the ammonia is expelled by the evaporation, there will be less ammonium chloride to burn out, and less danger of loss of sodium chloride by ignition. Continue the evaporation, and, when the mass is perfectly dry, ignite gently until vapor of ammonium chloride ceases to be evolved. Cool, dissolve in a little boiling water, and filter into a weighed platinum dish; washing the filter until a few drops of the wash-water do not give a precipitate of silver chloride, when treated with silver nitrate. Then evaporate the filtrate to dryness, ignite gently, and weigh the sodium chloride. From this weight, calculate the per cent of soda. The ignited sodium chloride should be white and perfectly soluble in water. If it is not, filter the solution, wash the insoluble residue, evaporate the filtrate and washings to dryness, ignite, and weigh again.

For the determination of phosphoric acid, take 1 gm. of the salt, weighed as directed in the analysis of potassium alum, or a portion of a solution of larger quantity equivalent to 1 gm. If 1 gm. of the solid salt is taken, dissolve it in 50 c. c. of cold water, acidify the solution with hydrochloric acid, and then make it slightly alkaline with ammonia. When the solution is cool, add gradually (best from a burette), with constant stirring, 12 c. c. of "magnesium mixture." The magnesium chloride (made ac-

cording to Gooch's formula, *vid.* p. 21) is now usually preferred. If the reagent is added too rapidly, the precipitate may be impure. Let stand for some time. After the precipitate has settled completely, filter, wash with dilute ammonia until the washings give no reaction with alkaline phosphate, and place the funnel containing the precipitate in an air-bath to dry. Reserve the filtrate for some hours. Should another precipitate appear, filter it out on the smallest-sized filter, wash it with 20 or 30 c. c. of dilute ammonia, dissolve it through the filter with a little dilute hydrochloric acid into a small beaker, and make the solution alkaline with ammonia. If the ammonia produces a precipitate, filter it out, wash it with dilute ammonia, dry, and ignite with the main precipitate of ammonio-magnesium-phosphate. Ignition converts this into magnesium pyrophosphate. From this, after weighing and deducting the weight of the crucible and filter-ash, calculate the per cent of P_2O_5 . It sometimes happens that, in precipitation of phosphoric acid by means of magnesia mixture, some magnesium hydrate is precipitated with the phosphate. When there is reason to suspect that such has been the case, from the flocculent appearance of the precipitate, dissolve the ignited precipitate of pyrophosphate in a little hydrochloric acid, dilute slightly, add a few drops of nitric acid, and boil gently for about an hour, renewing the fluid from time to time. By this means, the pyrophosphoric acid will be converted into the tribasic acid again. Then make the fluid alkaline with ammonia. The ammonio-magnesium-phosphate will be precipitated free from magnesium hydrate, and is to be treated as directed above. It is necessary to convert the pyrophosphoric or tetrabasic into the tribasic acid before adding the ammonia, as the pyrophosphate is soluble to an appreciable extent in ammonia water.

For the determination of the water, weigh 1 gm. of the phosphate in a boat made of platinum foil. Introduce the boat into a tube of hard glass about 8 or 10 inches long,

such as is used for combustion in organic analysis. One end of this tube is closed by a cork, through which passes a short piece of smaller glass tubing, while the other end is drawn out to a long point, bent at a right angle to the body of the tube. Insert the point into an ordinary calcium chloride tube previously filled and weighed, letting it project a short distance through the cork. This arrangement is designed to afford an uninterrupted passage of the water from the ignition-tube into the calcium chloride, and allow the application of heat very near the extreme point of the ignition-tube, to drive all the water into the absorption-tube containing anhydrous calcium chloride. Connect the cork for the other end of the ignition-tube by means of rubber with another tube containing calcium chloride. This latter is intended to dry the air drawn through the apparatus. After the boat containing the substance is introduced into the ignition-tube, insert the cork, attach the weighed absorption-tube to the point, connect the other end of the absorption-tube by means of rubber tubing with an aspirator, and proceed to draw a gentle current of air through the apparatus. Then apply heat to the ignition-tube sufficient to expel the water. When this is all drawn into the absorption-tube detach the aspirator, allow the apparatus to cool, and weigh the absorption-tube. The increase in weight will be equivalent to the weight of water. From this, calculate the per cent as usual.

NOTE.—The soda may also be determined as sulphate. To a solution of about 1 gm. of the salt, add 2 gms. of pure crystallized ferrous sulphate, dilute to about 200 c. c., boil, and then add strong nitric acid drop by drop, until the iron is completely oxidized, as found by testing a drop or two with potassium-ferricyanide. Then add to the hot solution ammonia in slight excess, which precipitates out ferric hydrate and phosphate together. Filter, and wash until a few drops of the washings evaporated and ignited on platinum foil leave practically no residue. Boil down the solution in a casserole. When in small bulk, transfer to a weighed platinum dish, evaporate to dryness, and ignite cautiously. If the mass is colored, or partially insoluble in water, dissolve in a little water, filter to remove impurities, evaporate, ignite, and weigh what should now be pure Na_2SO_4 .

CHAPTER IX.

AMMONIO-FERRIC SULPHATE, OR AMMONIA IRON ALUM.



The theoretical composition of the salt is :

Fe ₂ O ₃	16.60 per cent.
SO ₃	83.20 " "
NH ₃	3.52 " "
H ₂ O.....	46.68 " "
	100.00

Select 8 or 10 gms. of crystals which have not lost water by efflorescence ; break them into small pieces or coarse powder, and keep for analysis in a small, well-corked bottle. Consult analysis of hydro-disodium phosphate.

For the determination of the ferric oxide by precipitation, take as nearly as possible 1 gm. weighed in the manner directed in the analysis of potassium alum, or an equivalent amount from the solution of a larger quantity, if the plan suggested in the analysis of hydro-disodium phosphate be adopted.

If 1 gm. of the solid salt be weighed, dissolve it in 100 c. c. hot water and 1 c. c. dilute hydrochloric acid. When the solution is complete, add ammonia in excess so as to render the solution decidedly alkaline, and heat to boiling. Then remove the heat and allow the precipitate to settle ; decant the clear fluid through a filter, pour upon the precipitate 50 c. c. hot water, stir, allow the precipitate to settle, and pour the clear fluid through the filter as before. Repeat this washing by decantation three times. Then transfer the precipitate to the filter with hot water, and wash with hot water until the washings give no precipitate when treated with barium chloride solution. Dry the precipitate thoroughly, and remove it from the filter

by inverting the latter on a clock-glass, and rubbing the filter between the fingers. By this means, nearly all of the precipitate can be removed from the filter, without any danger of loss by brushing. After removing the precipitate as cleanly as possible, burn the filter in a weighed crucible, after adding a few drops of nitric acid. When the carbon of the filter is completely consumed, brush the precipitate into the crucible, and ignite again, keeping it covered until all danger of decrepitation is past. Then remove the cover, and heat to a bright red heat. After heating intensely for some minutes, remove the heat, cool the crucible and contents in a desiccator, and weigh. From this weight, we obtain the per cent of Fe_2O_3 by deducting the weight of crucible and filter-ash. If the contents of the crucible should look black, moisten with a few drops of nitric acid, evaporate off the excess of acid carefully, ignite, cool, and weigh again.

For the determination of the SO_3 , acidulate the filtrate from the ferric hydrate, and proceed as in the analysis of magnesium sulphate.

To determine the ferric oxide by ignition, introduce about 1 gm. of the salt into a previously-weighed crucible, and heat gently, and then gradually increase the heat to the highest point attainable over a blast-lamp. Cool and weigh. Repeat until the weight becomes constant. The expulsion of the sulphuric acid can be facilitated by introducing into the crucible a piece of pure ammonium carbonate about the size of a pea, covering the crucible, and heating moderately until the ammonium carbonate is volatilized, and then strongly, as before. Only ferric oxide will be left. Calculate the per cent as usual.

Of the various methods suggested for the determination of iron volumetrically, it is unnecessary to notice more than two, namely, that turning upon the use of potassium permanganate, and that in which potassium bichromate is employed.

The first method, known as Marguerite's, depends upon

the fact that a solution of potassium permanganate, which is intensely colored, loses its color when dropped into a solution of ferrous oxide, giving up a portion of its oxygen, and being decomposed into salts of manganese and potassium, until the ferrous is completely converted into ferric oxide. The moment this conversion is complete, the permanganate imparts color to the fluid.

The analysis requires a standard solution of potassium permanganate, that is, one the value of which is known.

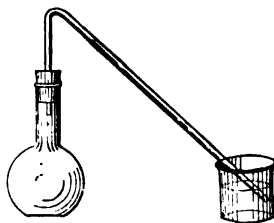
To prepare this solution, dissolve 3.000 gms. of pure crystals of potassium permanganate in 1 litre of distilled water, with frequent agitation to insure complete solution, if possible. After this, allow the fluid to stand for 24 hours, and siphon off into another vessel the perfectly clear solution, and close this tightly with a stopper, preferably of glass.

There are several methods of standardizing the solution of potassium permanganate. Of these, only two will be described as reliable, namely, by means of iron, or by oxalic acid. Of these, the former (the method proposed by Marguerite) is the better one. Use for the purpose fine piano-forte wire, which contains 99.7 per cent of iron. Dissolve 0.200 gm. of the wire—previously cleaned with sand-paper to remove oxide, glaze, and dirt—in a small valved flask, with 25 or 30 c. c. of dilute sulphuric acid, by the aid of gentle heat; introducing into the flask, with the wire, a small crystal of sodium carbonate, about as large as a hemp-seed; by which means the atmospheric air will be displaced by carbonic acid, thus preventing the formation of ferric oxide during the solution. When the iron is dissolved, allow the flask and contents to cool slowly. Do not attempt to hurry the cooling by the application of any cold substance, as the sudden formation of a partial vacuum may crush the flask and scatter the contents.

A very convenient kind of valve for the flask in which the iron wire is dissolved is the Kroonig valve, described

by Mohr in his *Titrimethode* (5th ed., 1877, p. 182), which is made of a piece of thick rubber tubing, about one and a half inches long, one end of which is forced over a short glass tube, passing through the cork into the neck of the flask, while the other end is closed by a short piece of glass rod. The rubber tube has a longitudinal slit cut in it between the end of the piece of glass rod and the glass tube. When the pressure is internal, the slit opens, allowing the gas and vapor to escape, and it closes when the pressure is external, owing to the cooling of the flask, thus preventing the entrance of oxygen.

Another efficient device for excluding air while dissolving the iron consists in the "water seal," made by adapting to the cork in the flask a tube bent as shown. The other end of the tube dips into a vessel of water. The hydrogen and steam from the boiling expel the air, which bubbles up through the water. Eventually only steam escapes, which condenses at once. When the wire is entirely dissolved, withdraw the heat, and allow the water to be drawn back into the flask.

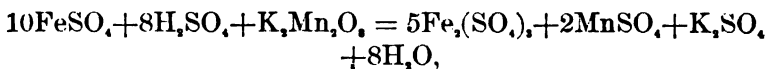


Allow the iron solution to cool; meantime fill a burette with some of the permanganate solution. The burette should be of such a pattern that the solution only comes in contact with glass. Contact with rubber, cork, etc., causes it to alter in strength rapidly. Empty the contents of the flask into a beaker, add 30 to 50 c. c. of diluted sulphuric acid, and with the rinsings of the flask bring the bulk up to about 500 c. c. Then run in the permanganate solution from the burette with stirring, rapidly at first, afterward slowly, until finally one drop gives a faint pink tinge to the solution, which is permanent for at least one minute. Note the quantity of permanganate solution used, and calculate the value of 1 c. c. thus: Suppose the weight of the iron wire was 0.2 gm. Assuming it to contain 99.7

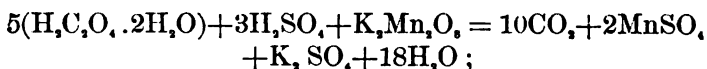
per cent of iron, this would represent 0.1994 gm. iron. Divide this by the number of cc. of permanganate used. Suppose that were 39.8 c. c.; 0.1994 divided by 39.8 gives 0.00501 Fe for the value of 1 c. c. Since the ratio of Fe₂ to Fe₂O₃ is 112 : 160 = 7 : 10; the value of 1 c. c. in Fe₂O₃ is obtained by changing the decimal point, and dividing by 7. In this case 1 c. c. = 0.007157 Fe₂O₃.

To standardize the potassium permanganate solution by means of oxalic acid, dissolve some pure crystallized oxalic acid (H₂C₂O₄.2H₂O) in the proportion of 6.3 gms. per litre. Take 25 c. c. of this solution (representing 0.1575 gm.), dilute to about 100 c. c., add 5 or 6 c. c. of strong sulphuric acid, and heat to about 60° C. The reaction will take place very slowly, unless about this temperature is reached. On the other hand, boiling is disadvantageous, since boiling dilute sulphuric acid has itself a tendency to decompose potassium permanganate.

Run in the permanganate solution from the burette as before, until the last drop imparts a permanent pink tinge to the solution. By comparing the equations representing the reactions, it will be seen that the same quantity of potassium permanganate is required to oxidize 1 molecule of oxalic acid, whose molecular weight is 126, or 2 atoms of iron (in the form of monoxide), whose molecular weight is 112. Thus, the following represents the oxidation of iron,



while the next one represents the oxidation of oxalic acid,



consequently, 630 : 560 = 0.1575 : 0.1400. In other words, one molecule of potassium permanganate will oxidize 560 parts of iron (equation 1), or 630 parts of crystallized oxalic acid (equation 2). The ratio of oxalic acid to iron is therefore 630 : 560 or 9 : 8, and the 0.1575 gm. oxalic acid taken

represents 0.1400 gm. iron. Calculate in the same manner as before.

In either standardizing or titrating a persistent brown tint in the solution indicates an insufficient amount of sulphuric acid, and the consequent formation of Mn_2O_3 compounds. If this cannot be removed by addition of more sulphuric acid, the results should be rejected as untrustworthy.

Whichever method of standardizing the permanganate solution is adopted, it is necessary to make more than one trial. Should the quantities of permanganate required in two trials not differ by more than one tenth of a cubic centimetre, the average of the two may be taken as correct. Should a greater difference than this occur, more trials must be made to obtain consistent results.

To determine the ferric oxide, weigh about 4 gms. of the ammonio-ferric sulphate, observing the precautions suggested before, transfer the substance to a flask holding 200 c. c., add 2 or 3 c. c. of sulphuric acid, and dilute to the mark. Mix well, and then divide the solution equally between two flasks (100 c. c. in each). The rinsings may be divided by guess.

Place in each flask a piece of platinum foil, and 20 to 50 gms. of amalgamated (granulated) zinc in pieces of about the shape and size of buckshot. Then on warming gently an active evolution of hydrogen should take place, the galvanic action causing solution of the zinc, and a simultaneous reduction of the iron to the ferrous form. If the platinum foil is new and bright, the action may not be so prompt as is desirable. In that case the addition of one or two drops of platinic chloride which causes a deposit of spongy platinum on the surface of the foils will usually remedy the difficulty.

Unamalgamated zinc can be used for the reduction of the iron, but in that case a blank test must be made, using approximately the same amounts of zinc and acid. By this means the results obtained may be corrected by

deducting the amount of permanganate required by the iron and other impurities in the zinc. When amalgamated, the iron (or impurity) in the zinc will not dissolve until almost all of the zinc is dissolved.

If the zinc is used in larger masses, it does not afford enough surface to cause a rapid reduction of the iron. If in smaller masses, some particles may become detached and float about in the solution, in consequence of the vigorous escape of gas from their surfaces. In such cases the solution must be filtered, after reduction is complete, through a rapidly running plaited filter containing a few fragments of zinc to keep up the action.

When the amalgamated zinc "shot" are used, the same lot of zinc will serve for several reductions, if well washed by decantation each time. The platinum foils used should be washed, and then heated to redness after each operation.

After warming for 15 or 20 minutes, tests should be made to determine whether *all* of the iron present has been reduced to the ferrous form. When this has been accomplished, the solution from the first flask should be decanted into a beaker, and the zinc washed by decantation three or four times with cold dilute sulphuric acid (about 1:20), the solution and washings being united in the beaker. The titration is conducted in the manner already described, and then the operation is repeated with the contents of the second flask.

The two titrations should not differ more than two tenths of a c. c. If they do, another determination should be made.

The Jones "reductor" (*Trans. Am. Inst. Min. Eng.*, XVII., 414) or a simplified form thereof (Dudley and Pease, *Jour. An. and App. Chem.* VII., 109) may be used for the rapid reduction of ferric solutions. The simplified "reductor" consists of a piece of combustion-tubing 12 or 14 inches long, fitted at one end with a cork carrying a funnel; and at the other end, connected with a filtration

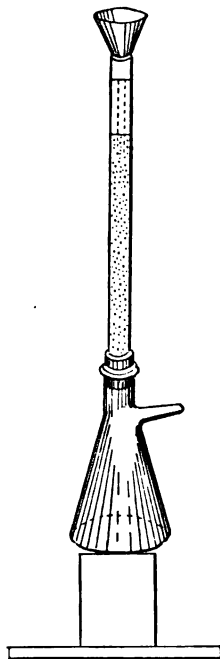
flask at the bottom of the combustion-tube, is placed a perforated platinum disk, on this about an inch of clean coarse quartz sand, then another perforated platinum disk, and on this finely divided zinc, with which the tube is filled nearly to the top.

The zinc is best prepared for this purpose by the method used in obtaining "granulated test lead" for fire assaying. Some zinc (spelter) is melted at as low a temperature as possible in a ladle or crucible and then poured into a wooden tray or box, which latter is shaken until the granules are too cool to adhere to one another. This material should be sifted, and the portion passing through a 20- or 30-mesh sieve taken for use in the "reductor."

The idea involved is that by passing a solution through such a column of zinc (with the aid of suction) one obtains a complete reduction at once, and the solution is ready for titration.

Before passing the solution to be tested, two or three blanks must be passed through the reductor. These blanks should have the same bulk, and contain the same amount of acid as the test solution; they should then be titrated.

The first blank, after the reductor has stood for a time, is likely to use up more permanganate than the subsequent ones. When two consecutive blank tests, after washing, etc., take the same amount of permanganate, this amount is to be noted, that it may be deducted for the iron or other impurity in the zinc. Then the solution of iron, suitably acidified with sulphuric acid (about 200 c. c. in bulk) is passed through the reductor, and followed by 100 to 200 c. c. of wash water; the solution is titrated, the correction made, and the amount of iron present is calculated.



In determining iron by titration with permanganate the presence of hydrochloric acid is disadvantageous, especially if the solution is concentrated or warm, since the hydrochloric acid itself will, under these conditions, destroy permanganate. The reaction is $\text{K}_2\text{Mn}_2\text{O}_8 + 16\text{HCl} = 2\text{KCl} + 2\text{MnCl}_2 + 8\text{H}_2\text{O} + 10\text{Cl}_2$.

Some of the chlorine may convert the ferrous salt into ferric, but some usually escapes, and the results become untrustworthy. In case of the presence of hydrochloric acid satisfactory results can only be obtained if the solutions both of iron and of permanganate are cold and dilute, and also if the sulphuric acid largely predominates (Krutwig and Cocheteux, *Berichte*, XVI., 1534). A more convenient way of avoiding error consists in adding to the iron solution, just before titrating, about 20 c. c. of a 20-per-cent solution of manganese sulphate (Zimmermann, *Berichte*, XIV., 779). The effect is a temporary formation of $\text{Mn}_2(\text{SO}_4)_3$, which retains the oxidizing influence induced by the permanganate in the solution.

The other method of determining iron volumetrically—by potassium dichromate—has the advantage that it is best effected in a hydrochloric-acid solution. The principle is the same, in that one measures the amount of solution of an oxidizing agent necessary to convert the iron present from the ferrous to the ferric form. The mode of determining the end of the operation (the "end-reaction") is not quite so convenient as with the permanganate.

The reaction is: $6\text{FeCl}_2 + \text{K}_2\text{Cr}_2\text{O}_7 + 14\text{HCl} = 3\text{Fe}_2\text{Cl}_6 + 2\text{KCl} + \text{Cr}_2\text{Cl}_6 + 8\text{H}_2\text{O}$. One molecule of dichromate or 294.42 parts will convert six molecules or 336 parts of iron from the ferrous to the ferric form. To obtain a solution, therefore, of which 1 c. c. = approximately 0.005 gm. Fe, it would be necessary to dissolve 4.3812 gms. of the dichromate in a litre of water. Before weighing out the salt, it should be well pulverized and dried in an air bath. Purification by fusing, as recommended by some, is objectionable, since some decomposition is sure to ensue. The solu-

tion may be standardized with iron wire, as in the case of the permanganate, using lots of about 0.200 gm. each, which should be dissolved in about 30 c. c. of dilute hydrochloric acid in a valved or "water-sealed" flask. After solution has been effected, pour the solution into a beaker, rinse out once or twice with hot water, and titrate hot.

The fact that the solution needs to be hot, and also that the ferrous chloride oxidizes more rapidly in contact with the air than does ferrous sulphate, suggest reasons for working quickly at this stage. On adding the dichromate (from a burette) the solution at once turns green from formation of chromium chloride. Should it turn brown, more hydrochloric acid is needed. When it is judged that nearly enough of the dichromate has been added, take out a drop of the solution on a glass rod, and place it on a white porcelain plate in contact with a drop of dilute solution of potassium ferricyanide ("red prussiate"). If a blue precipitate forms, the titration is unfinished. Continue adding the dichromate solution cautiously, and in small quantities toward the last, until a drop of the solution gives no blue with the ferricyanide solution, indicating that no more ferrous iron remains; then take the reading of the burette. From the number of c. c. used, calculate the strength of the solution.

Especial care must be used in the selection of the potassium ferricyanide for this test. Much of the material sold by dealers contains potassium ferrocyanide (which gives a blue with ferric salts) and is therefore useless; moreover, a solution of good potassium ferricyanide by standing becomes partially altered to ferrocyanide. Hence the reagent must be kept in the solid form, and a fresh solution made for the tests of each day, by dissolving two or three fragments, the size of the head of a pin, in 5 or 10 c. c. of water in a clock glass. It is well, just before beginning the titration, to "spot" the porcelain plate with the ferricyanide solution in ten or twenty places, to facilitate the tests on the progress of the titration.

In order to titrate a solution containing ferric salts, *e. g.*, that of the ammonia iron alum, the iron must first be reduced. For this purpose zinc is objectionable, since zinc ferricyanide in the "spot test" is liable to obscure the end reaction. The reducing agent preferred is stannous chloride ("tin salt"), and, in order to destroy the excess of stannous chloride, a solution of mercuric chloride is used.

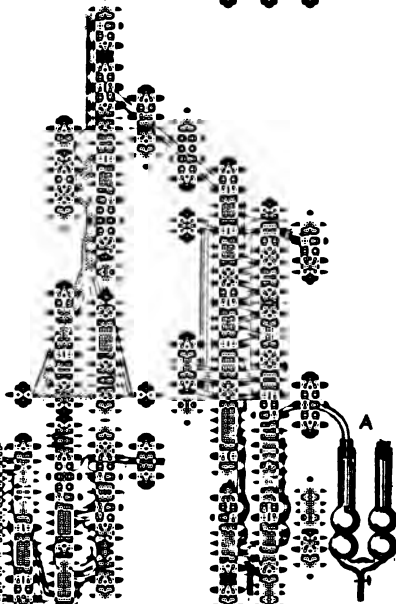
The stannous chloride solution should contain about 12 gms. of metallic tin per litre. The metal is dissolved in boiling concentrated hydrochloric acid, a strip of platinum foil being introduced to hasten solution by galvanic action. After dissolving, dilute to the proper volume, and keep the solution in a well-stoppered bottle, containing a few granules of tin at the bottom.

The mercuric chloride solution is made by dissolving 14 gms. of the salt in one litre of water.

To reduce the iron, add the tin solution from a tube or pipette rather slowly to the hot ferric solution, to which 10 or 20 c. c. of concentrated hydrochloric acid have been added. When the color begins to pale, add only a few drops at a time, and wait a few seconds between each addition, since the last portions of iron reduce comparatively slowly. The action is more rapid the more concentrated the solution. The reduction may be regarded as complete when the color imparted by the ferric salt is entirely discharged. If the solution has decidedly the green tint of ferrous chloride, the solution is too concentrated; it should be practically colorless. Then, without delay and *all at once*, pour in from a stand-glass 15 or 20 c. c. of the mercuric chloride solution. If the addition of the tin solution has been properly managed, a faint *white* crystalline cloud of mercurous chloride appears, and titration may be proceeded with. If too much tin solution has been used, a *gray black* cloud of finely divided mercury separates, and the titration cannot be made to yield accurate results.

It may be here suggested that besides iron wire and

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 6th Ed., p. 107.
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denser. For this purpose a worm condenser is preferable. The ends of the tubes should just touch one another and about an inch of (black) rubber tubing should cover the joint, to make it tight and hold them in place. It is not advisable to allow the steam containing ammonia to come in contact with any extended length of rubber tubing, as that may easily cause inaccuracies.

The delivery-tube of the condenser had best be connected with a bulb-tube, the joint being made as above. The lower end of the tube should dip under the surface of the water in a beaker (about 50 c. c.), to which 1 or 2 c. c. of strong hydrochloric acid has been added. Instead of a beaker, bulb tubes (*A*), or the bulbed Erlenmeyer flask (*B*), either containing diluted acid, may be attached. When all else is ready, introduce about 10 c. c. of strong solution of potassium hydrate through the Wurz tube, by means of a long-stemmed funnel, replace the cork quickly, and heat to boiling.

Distil over about half the contents of the flask, then test the steam with litmus-paper, momentarily withdrawing the cork for that purpose. If it is alkaline, replace the cork, and continue the distillation. When the steam is neutral to litmus-paper, disconnect the condenser, and rinse it out by a jet from the wash-bottle. Concentrate the contents of beaker (or receiver) and washings on the water-bath to small bulk (best in an evaporating-dish), add 5 c. c. of platinic chloride solution, and evaporate to a pasty condition. Then remove from the water-bath and add 50 c. c. of alcohol (90 per cent) and 15 c. c. of ether. Allow the dish to stand cold for about two hours, protecting it meantime from external influences by inverting a beaker over it or in some other way.

Filter as in the case of potassium (Chapter IV.), washing with a mixture of alcohol and (one-fourth) ether instead of alcohol alone. Weighed filters (Gooch) may be used, or the precipitate $[(\text{NH}_4)_2\text{PtCl}_6]$ may be ignited and the spongy platinum weighed. In the latter case, washing

after ignition (required in the case of potassium) is unnecessary, but especial caution is needed in igniting, since fine particles of platinum can be readily carried off with the ammonium chloride when volatilizing. The heat should be increased very slowly.

If alkalimetric and acidimetric solutions are at hand (*vid.* alkalimetry and acidimetry) the beaker or receiver may contain a measured amount (10 or 15 c. c.) of half-normal acid suitably diluted, and after the distillation is over, the acidity remaining may be determined by titrating with normal alkali, finishing the titration with tenth normal alkali. From the data thus obtained, the amount, and consequently the percentage, of ammonia may be calculated.

CHAPTER X.

FELDSPAR.

The following analyses, taken from Dana's *Mineralogy* show the composition of ordinary feldspar :

	Orthoclase.	Albite.
Silica.....	64.25	65.46
Alumina.....	18.80	20.74
Ferrous Oxide.....		0.54
Lime.....	1.20	0.71
Magnesia.....		0.74
Soda.....	2.40	9.98
Potash.....	12.44	1.80
Loss by ignition.....	0.80
	99.89	99.97

Pulverize 3 or 4 gms. of the feldspar very fine, in an agate mortar, and keep the powder in a small, corked bottle. Fuse over a good burner 1 gm. of this, carefully weighed, in a 2-oz. platinum crucible, intimately mixed with about 5 gms. of flux, composed of equal parts of potassium and sodium carbonates. The combined carbonates make a much more fusible flux than either alone. Examine the crucible occasionally, and, when the contents are fused so to flow when the crucible is inclined, move it about, after laying the cover aside in a convenient place, in such a way as to cause the contents to coat the sides, instead of cooling in a solid mass at the bottom, and dip it, while still hot, into a beaker of cold water, to about half of its depth. Hold it in the water for a few seconds, remove it, and, after the lapse of a few more seconds, dip it again. Repeat this treatment until the crucible and contents are cool enough to immerse without spattering. Then lay the crucible on its side in the beaker, which should be just large enough to permit this, and have in it

a sufficient quantity of water barely to cover the crucible. Then put the lid also in the beaker, and, after placing a convex glass over it, allow it to stand until the fused mass is sufficiently softened to be removed from the crucible. Owing to the contraction and expansion caused by this treatment, the mass can frequently be removed at once from the crucible in thin cakes. The water solution, before acidifying, should be made up to a bulk of 400 to 500 c. c., and when acidified the acid should be added little by little, avoiding, so far as possible the formation of a precipitate of gelatinous silica at this stage. This method, although requiring more time for evaporation, affords a purer precipitate, and one which filters, and is washed more readily than that obtained by other methods (so-called "vitreoussilica"—*vid.* Lindo, *Ch. News*, LX., 14; also Gilbert, *J. Anal and App. Chem.*, IV., 159). After removing the substance from the crucible, place the latter, with the cover, in another vessel, pour on them a little dilute hydrochloric acid, to dissolve any adhering particles, and wash them with water. Pour this solution cautiously into the vessel containing the fused feldspar, keeping it covered with a glass, to prevent loss by effervescence, and add more hydrochloric acid, if necessary, a little at a time. When the fluid is acid, heat until all carbonic acid is expelled. Then, if the mineral is entirely decomposed, transfer all to a casserole, and evaporate on a water-bath to dryness. Then heat in an air-bath at a temperature of from 100° to 110° C. until the odor of hydrochloric acid disappears. Should there be any undecomposed mineral, allow it to settle, decant the clear fluid into a casserole, and begin to evaporate it as above. In the mean time, add some strong hydrochloric acid to the residue, and heat to dissolve it if possible. Should it dissolve, add the solution to the first one. Should it not dissolve, dilute with a little water, filter, wash, and add the filtrate to the principal solution. Dry the insoluble residue, burn it with the filter in a platinum crucible, fuse it with about five

times its weight of mixed carbonates, as in the first case, and treat as directed above. Repeat the treatment until the feldspar is all decomposed. Undecomposed mineral can be detected by the rapidity with which it settles to the bottom of the fluid, and by feeling hard and gritty when pressed by a glass rod, while separated silica rises readily in the solution when agitated, settles slowly, and offers no resistance to the rod. After the mass is thoroughly dried, moisten it with 20 c. c. dilute hydrochloric acid, heat at a temperature just below boiling for 20 or 30 minutes, and dilute with 50 c. c. hot water; every thing should now be in solution except the silica. Now filter out the silica, wash it with hot water until the washings give no reaction for chlorine, when treated with silver nitrate, and dry the precipitate on the filter, at a temperature of from 100° to 110° C. When the silica is perfectly dry, invert the filter in a weighed platinum crucible, standing on a sheet of glazed paper, roll the filter gently between the fingers in such a way as to remove the contents from the paper to the crucible, and, without lifting the filter from the crucible, fold it and press it carefully down upon the silica. After brushing into the crucible any particles that may have fallen on the paper, put on the cover, and ignite at first at a heat not more than sufficient to char the paper. Continue the low heat as long as smoke emerges from the crucible. After all volatile matter has been expelled, incline the crucible on the support, and gradually raise the heat to the highest point attainable by means of a good burner, keeping the cover on for a few minutes. Finally, remove the cover, and continue heating until the carbon of the filter is consumed and the silica is white. Then cool the crucible and contents in a desiccator, weigh, and calculate the per cent of silica, which still retains, perhaps, a little alumina. After weighing, moisten the contents of the crucible with pure concentrated sulphuric acid, add about 1 gm. of ammonium fluoride, which leaves no residue after ignition, incline the

crucible on the support, replace the cover, and apply the heat of a burner in such a way that the flame will strike the edge of the crucible and lid. When the sulphuric acid is expelled, heat the whole crucible strongly, cool, and weigh it. Repeat this treatment until the crucible ceases to lose weight. The loss represents silica expelled as silicon fluoride. If any thing remains in the crucible, fuse it with a little acid potassium, or sodium sulphate, cool, moisten with sulphuric acid, and heat again, until the mass becomes fluid. Finally, cool and dissolve in water, and add the solution to the filtrate from the silica.

Rapid ignition in the first instance, will cause loss of silica, as its particles, being very minute and light, are liable to be carried off by the gases expelled from the filter-paper by combustion, and also by the vapor of the water remaining in the silica itself after drying, since all moisture can not be expelled from it by drying at a temperature which will not destroy the fibre of the filter.

To determine the alumina, add to the filtrate from the silica, ammonia until the fluid is slightly alkaline, and proceed as directed in the analysis of potassium alum.

If there be any oxide of iron in the feldspar, it will be found in the precipitate of alumina, in which case fuse the ignited precipitate with pure potassium hydrate, preferably in a silver crucible, digest the fused mass until it is reduced to a pulverized form, and entirely removed from the crucible, which is to be washed and removed. Digest again, until the alumina is dissolved in the alkaline fluid, and only ferric hydrate remains. Filter, wash well, dry, ignite, and weigh the ferric oxide. Its weight, deducted from the known weight of alumina and ferric oxide combined, gives the weight of the alumina; or the alumina may be determined directly by acidifying the alkaline solution with hydrochloric acid, then making it alkaline with ammonia, boiling, and determining the alumina as before, as directed in the analysis of potassium alum.

To determine the ferric oxide by titration, fuse the ignited precipitate of alumina containing ferric oxide, with 6 or 8 times its weight of acid potassium sulphate; until the second molecule of sulphuric acid is expelled; cool, add a volume of pure concentrated sulphuric acid equal to that of the fused mass, heat again carefully, until the contents of the crucible become fluid. Then cool, place the crucible in a vessel of hot water, and digest over heat until the sulphates are dissolved. Then reduce with zinc and platinum, and titrate with potassium permanganate, as directed in the analysis of ammonio-ferric sulphate, and calculate the per cent of ferric oxide. If this method is adopted, the alumina is, of course, to be determined by difference.

To determine the lime and magnesia, treat the filtrate from the precipitate of alumina and ferric oxide as directed in the analysis of limestone.

The best method of determining the sodium and potassium is that of Professor J. Lawrence Smith (*Am. Jour. Sci. and Arts*, Vol. I., 1871, p. 269) for separating the alkalies from silicates. The method is described in his own words: "The silicate is to be well pulverized in an agate mortar; for the analysis I take $\frac{1}{2}$ gm. or 1 gm.; the former is most commonly used, as being sufficient, and best manipulated in the crucible used; a gramme, however, may be conveniently employed. The weighed mineral is placed in a large agate mortar, or, better, in a glazed porcelain mortar, of $\frac{1}{2}$ to 1 pint capacity. Weigh out an equal quantity of granular sal-ammoniac (a centigramme more or less is of no consequence), put it in the mortar with the mineral, rub the two together intimately; after which, add 8 parts of carbonate of lime, in three or four portions, and mix intimately after each addition; empty the contents of the mortar completely upon a piece of glazed paper, that ought always to be under the mortar, and introduce into the crucible. The crucible is tapped gently upon the table and the contents settled down.

"It is then clasped by a metallic clamp in an inclined position, or it is placed in the support referred to in the latter part of this article, leaving outside about $\frac{1}{2}$ or $\frac{3}{4}$ inch ; a small Bunsen burner is now placed beneath the crucible, and the heat brought to bear just about the top of the mixture, and gradually carried toward the lower part, until the sal-ammoniac is completely decomposed, which takes about 4 or 5 minutes ; heat is then applied in the manner suggested, either with the blast or with the burner referred to, acting by its own draught, and the whole kept up to a bright red heat for about from 40 to 60 minutes. It is well to avoid too intense a heat, as it may vitrify the mass too much. The crucible is now allowed to cool, and when cold, the contents will be found to be more or less agglomerated, in the form of a semi-fused mass. A glass rod, or blunt steel point, will most commonly detach the mass, which is to be dropped into a platinum or porcelain capsule, of about 150 c. c. capacity, and 60 or 80 c. c. of distilled water is added. In the course of a longer or shorter space of time, the mass will slake and crumble after the manner of lime ; still better, this may be hastened by bringing the contents of the capsule to the boiling-point, either over a lamp or water-bath. At the same time, water is put into the crucible, to slake out any small particles that may adhere to it, and, subsequently, this is added to that in the capsule, washing off the cover of the crucible also.

"After the mass is completely slaked, the analysis may be proceeded with, although, as a general thing, I prefer to allow the digestion to continue 6 or 8 hours, which, however, is not necessary. If the contents of the crucible are not easily detached, do not use unnecessary force, as the crucible may be injured by it, but fill the crucible to about two thirds of its capacity with water, bring almost to the boiling-point, and lay it in the capsule, with the upper portion resting on the edge ; the lime will slake in the crucible, and then may be washed thoroughly

into the dish, and, as before, the cover is to be washed off.

“We have now, by this treatment with water, the excess of lime slaked into a hydrate, and some of the lime, combined with the silica and other ingredients of the silicate, in an impalpable form; in solution there is the excess of the chloride of calcium formed in the operation, and all the alkalies originally contained in the mineral as chlorides, and all that now remains to be done is to filter, separate the lime as carbonate, and we have nothing left but the chlorides of the alkalies. To do this I proceed as follows :

“Throw the contents of the capsule on a filter (the size preferred for the quantity above specified is one 3 to 3½ inches in diameter), wash well, to do which requires about 200 c. c. of water; the washing is executed rapidly. The contents of the filter (except in those cases where the amount of the mineral is very small, and there is no more for the estimation of the other constituents) is of no use, unless it be desired to heat again, first adding a little sal-ammoniac to see if any alkali still remains in it, a precaution I find unnecessary. The filtrate contains, in solution, all the alkalies of the mineral, together with some chloride of calcium and caustic lime; to this solution, after it has been placed in a platinum or porcelain capsule, is added a solution of pure carbonate of ammonia (equal to about 1½ gms. is required). This precipitates all the lime as carbonate; it is not, however, filtered immediately, but is evaporated over a water-bath, to about 40 c. c., and to this we add again a little carbonate of ammonia, and a few drops of caustic ammonia, to precipitate a little lime that is re-dissolved by the action of the sal-ammoniac on the carbonate of lime. Filter on a small filter (2 inches), which is readily and thoroughly washed with but a little water, and the filtrate allowed to run into a small beaker glass. In this filtrate are all the alkalies as chlorides, and a little sal-ammoniac; add a drop of a solution of carbon-

ate of ammonia, to make sure that no lime is present. Evaporate over a water-bath in a tared platinum dish, in which the alkalies are to be weighed; the capsule used is about from 30 to 60 c. c. capacity, and during the evaporation is never filled to more than two thirds its capacity. After the filtrate has been evaporated over the water-bath to dryness, the bottom of the dish is dried, and, on a proper support, heated very gently, by a Bunsen flame, to drive off the little sal-ammoniac. It is well to cover the capsule with a piece of thin platinum, to prevent any possible loss by the spitting of the salt after the sal-ammoniac has been driven off. Gradually increasing the heat, the temperature of the dish is brought up to a point a little below redness, the cover being off (the cover can be cleansed from any sal-ammoniac that may have condensed by heating it over the lamp). The capsule is again covered, and when sufficiently cooled, before becoming fully cold, is placed on the balance and weighed. This weight gives, as chlorides, the amount of alkalies contained in the mineral. If chloride of lithium be present, it is necessary to weigh quickly; for this salt, being very deliquescent, attracts moisture rapidly. It not unfrequently occurs that the chlorides, at the end of the analysis, are more or less colored with a small quantity of carbon, arising from certain constituents in carbonate of ammonia; the quantity is usually very minute, and in no way affects the accuracy of the analysis. In selecting pure carbonate of ammonia for analytical purposes, it is well to select specimens that are not colored by the action of light. It only now remains to separate the alkalies by the known methods."

The crucible and burner employed by Professor Smith in separating the alkalies from silicates are of his own devising, and excellent for the purpose. A description and drawing of them will be found in Crooke's *Select Methods*, p. 409, in the chapter on decomposition of silicates.

To separate the sodium and potassium and determine

them, dissolve the combined chlorides (after weighing them) in 20 or 30 c. c. of warm water. Should the solution be complete, transfer the solution to a small porcelain dish, add 3 or 4 drops of hydrochloric acid, and as much solution of platinum tetrachloride as contains an amount of the salt equivalent in weight to four times that of the combined chlorides present, and determine the potassium as directed in the analysis of potassium alum. Should the combined chlorides not go completely into water solution, filter, evaporate the filtrate in a platinum dish as before, and proceed as directed above. The solution in water must be complete. Any insoluble residue can not be alkaline chloride, and as the sodium is estimated by difference, it would falsify the results. Deduct the weight of potassium found, calculated to potassium chloride, from the weight of the combined chlorides. The difference will be sodium chloride. Calculate the per cent of K_2O and Na_2O .

Ignite 1 gm. of feldspar, and from loss calculate per cent of moisture and organic matter.

Lithium is sometimes found in feldspar. When such is the case, it is to be looked for in the solution of the alkaline chlorides.

Make the solution slightly acid, evaporate to dryness at $120^{\circ}C.$, add a mixture of equal parts of absolute alcohol and anhydrous ether, wash into a flask with the same, digest for 24 hours, shaking occasionally, decant on a filter, and treat with smaller quantities of the mixture of alcohol and ether. Finally, wash on the filter, with the same mixture, until the residue gives no evidence of the presence of lithium before the spectroscope. (*Pogg. Anal.*, 66, 79.)

As some sodium and potassium chlorides may be dissolved with the lithium chloride, evaporate off the alcohol and ether at low heat, just to dryness, and treat the impure lithium chloride in the same way. Should any residue of sodium and potassium chloride be left undis-

solved, filter it out, and add it to the first one. To the alcoholic solution add 20 or 30 c. c. of water, and boil out the alcohol and ether, add to the solution a sufficient quantity of pure sodium phosphate, and enough pure sodium hydrate to keep the reaction alkaline, and evaporate the mixture to dryness; pour water over the residue, in sufficient quantity to dissolve the soluble salts with the aid of a gentle heat, add an equal volume of ammonia, digest at a gentle heat, filter after 12 hours, and wash the basic phosphate of lithia with a mixture of equal volumes of water and ammonia. Evaporate the filtrate and washings to dryness, and treat the residue in the same way as before. Should any more lithium phosphate be obtained, add this to the principal quantity. Dry the precipitate, brush it from the filter as perfectly as possible into a clock-glass, burn the filter in a weighed crucible, add the precipitate, and ignite again, at a moderate red heat. Cool and weigh the basic lithium phosphate (Li_2PO_4).

Dissolve the residue of sodium and potassium chlorides in water, and treat as before for the determination of sodium and potassium, when no lithium is present.

If the weight of the combined chlorides is 0.200 gm. or less, the lithia may be separated and determined by the use of amyl alcohol. (Gooch's method, *Am. Chem. Jour.*, IX. 33.)

CHAPTER XI.

LIMESTONE.

The stone may contain lime, magnesia, iron, alumina, silica, carbonic acid, sulphur, phosphoric acid, water, and organic matter, also manganese, chlorine, fluorine, alkalies, and even other constituents in minute quantities. The lime may exist as carbonate or sulphate, the magnesia as carbonate or silicate, the iron as sulphide (pyrites) or oxide, and the silica as quartz or as silicic acid combined with bases.

The more common constituents, and those required to be determined for technical purposes, are lime, magnesia, alumina, iron, silica, carbonic acid, phosphoric acid, and sulphur.

For an analysis of this character, dry a few gms. of the finely pulverized stone, to constant weight at 150° C., and keep it in a stoppered bottle. Weigh 1 gm. of the dry powder, transfer it to a small beaker, add 20 c. c. of water, cover the beaker with a convex glass, add 2 c. c. of concentrated hydrochloric acid, two drops of concentrated nitric acid, and heat slowly to boiling. Filter, and wash with 30 or 40 c. c. of hot water, and proceed at once to evaporate the filtrate and washings over a water-bath. Dry the filter and any undissolved residue, ignite them in a small platinum crucible until the carbon of the filter is entirely consumed, add half a gramme of mixture of equal parts Na_2CO_3 and K_2CO_3 , and fuse until the contents of the crucible are fluid. Remove the fused mass from the crucible with water, dissolve off any adhering particles with hydrochloric acid, and add the solution to the vessel containing the principal contents of the crucible, keeping it covered to avoid loss by effervescence, also adding more

hydrochloric acid if necessary to render the solution acid. Boil out free carbonic acid, and combine with the principal solution on the water-bath. Evaporate all to dryness, transfer to an air-bath, and heat at a temperature of about 110° C. until the odor of hydrochloric acid disappears. Then add 1 c. c. of concentrated hydrochloric acid, and 20 c. c. of water, heat to incipient boiling, dilute with 50 c. c. of water, filter, and wash with hot water, until the washings show no turbidity when treated with silver nitrate (using only 2 or 3 drops of the wash-water at a time, and not beginning to test until 40 or 50 c. c. of it have passed through the filter). Dry the funnel and contents in an air-bath, at a temperature of about 110° C., ignite in a weighed crucible (observing the precautions given in the analysis of feldspar), cool, and weigh the silica.

To the filtrate from the silica, add ammonia to alkaline reaction, to precipitate the aluminum and ferric hydrates, boil out excess of ammonia and filter. Then dissolve the precipitate in hot dilute HCl, running the solution into the beaker in which precipitation was effected. Wash completely all acid from the filter-paper, and reprecipitate with ammonia as before. Use the same filter for the second precipitate, and combine the filtrates, etc. Then wash, dry, and weigh the alumina and ferric oxide together. Consult analysis of potassium alum, and that of ammonia-iron-alum.

If it be desired to determine the alumina and ferric oxide separately, proceed as directed in the analysis of feldspar.

Should the filtrate and washings from the hydrates exceed 100 c. c., concentrate to that bulk, if possible, and add 1 c. c. of ammonia. If the ammonia produce a precipitate other than aluminum or ferric hydrate, acidify the solution with hydrochloric acid, boil for a minute, and then make it nearly alkaline with ammonia. This is done to introduce a sufficient amount of ammonium chloride to prevent the precipitation of magnesium hydrate. Then add 40 c. c. of a solution of ammonium oxalate (pre-

pared by dissolving 1 part of the oxalate in 24 parts of water), enough to precipitate all the lime as oxalate, and convert the magnesia also into oxalate, which remains in solution. Fresenius says this excess is absolutely indispensable to insure complete precipitation of the lime, as calcium oxalate is slightly soluble in magnesium chloride, not mixed with ammonium oxalate. (See his *Experiment* number 92.) After adding the ammonium oxalate, heat just to boiling and allow the fluid to stand undisturbed for a short time. After the precipitate has settled perfectly, decant the clear fluid through a filter, wash by decantation once with about 25 c. c. of hot water, and set this filtrate aside as filtrate No. 1. Then dissolve the precipitate of calcium oxalate (mixed with a little magnesium oxalate) in the beaker, with as little hot dilute hydrochloric acid as possible. Should any of the precipitate have passed over on the filter, wash it back into the acid solution, make alkaline with ammonia, add a few drops of ammonium oxalate solution, and heat on the water-bath until the precipitate granulates and the solution "clears." When it has perfectly subsided, filter through the previous filter, transfer the precipitate to the same, wash it thoroughly with hot water, and determine the lime as directed in the analysis of calcium carbonate.

The first filtrate contains the larger portion of the magnesia, and the second the remainder. (See Fres., *Experiment* number 93.) Acidify the *second* filtrate and washings with hydrochloric acid, concentrate to small bulk, and add it to the first. Do not attempt to concentrate the first filtrate.

To determine the magnesia, make the combined filtrates from the calcium oxalate alkaline with ammonia, if not already so, add 30 c. c. of the ordinary solution of hydrodisodium phosphate, and determine the magnesia as directed in the analysis of magnesium sulphate.

To insure the recovery of all the magnesium, either evaporate the filtrate from the magnesium phosphate to

dryness, in a platinum dish, burn out the ammonium chloride, dissolve the residue in water containing a few drops of hydrochloric acid, and proceed as in the first instance; or, concentrate to small volume, add 4 or 5 c. c. strong nitric acid, evaporate to dryness, add 4 or 5 c. c. strong hydrochloric acid, evaporate nearly dry, dissolve in water, and determine magnesium as before.

(See J. Lawrence Smith, in *Am. Chem.*, Vol. III., p. 201.)

Determine the carbonic acid by one of the methods given in analysis of calcite; or, if the stone contains no organic matter, fuse 4 gms. vitrified borax in a platinum crucible, cool and weigh, then transfer 1 gm. of pulverized and well-dried stone to the crucible, and weigh again. Then heat gradually to redness, and continue until all is fused; cool and weigh. The loss of weight is carbonic acid. (See Fres., § 139.)

To determine the sulphur, dissolve 5 gms. in a mixture of 15 c. c. of strong hydrochloric acid, 5 c. c. of strong nitric acid, and 10 c. c. of water, in a covered casserole, heat to boiling, and when effervescence ceases, remove the cover, add 10 c. c. strong hydrochloric acid, and evaporate to dryness to expel nitric acid. Then add to the dry mass 1 c. c. of concentrated hydrochloric acid and 50 c. c. of water, and heat just to boiling. Filter out any residue, and wash with about 50 c. c. of hot water. Nearly neutralize the filtrate with ammonia, add 2 c. c. of barium chloride solution (containing 1 part of the salt in 10 parts of water), treat the precipitate of barium sulphate as in the analysis of magnesium sulphate, and calculate the sulphur.

To determine the phosphoric acid, dissolve 5 gms. of the stone in 10 c. c. of strong nitric acid, and 30 c. c. of hot water, in a casserole covered with a convex glass. When effervescence ceases, remove the cover, and evaporate to dryness. To the dry mass add 5 c. c. of strong nitric acid, and 50 c. c. of water, and boil. Then filter, wash with about 50 c. c. of water, nearly neutralize with ammonia,

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The first filtrate contains the larger portion of the magnesia, and the second the remainder. (See Fres., *Experiment* number 93.) Acidify the *second* filtrate and washings with hydrochloric acid, concentrate to small bulk, and add it to the first. Do not attempt to concentrate the first filtrate.

To determine the magnesia, make the combined filtrates from the calcium oxalate alkaline with ammonia, if not already so, add 30 c. c. of the ordinary solution of hydrodisodium phosphate, and determine the magnesia as directed in the analysis of magnesium sulphate.

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dryness, in a platinum dish, burn out the ammonium chloride, dissolve the residue in water containing a few drops of hydrochloric acid, and proceed as in the first instance; or, concentrate to small volume, add 4 or 5 c. c. strong nitric acid, evaporate to dryness, add 4 or 5 c. c. strong hydrochloric acid, evaporate nearly dry, dissolve in water, and determine magnesium as before.

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add 25 c. c. of molybdic acid solution, and allow to stand for some hours in a warm place. Should a yellow precipitate appear, filter it out, and wash it with molybdic acid solution (diluted with an equal volume of water). Dissolve the precipitate through the filter into a small beaker with the smallest possible amount of dilute ammonia, add 2 c. c. of magnesium mixture, and proceed as directed in the analysis of hydro-disodium-phosphate. Should a second precipitate appear in the filtrate from the first precipitate of phospho-molybdate, filter it out and treat it in the same way. Calculate the per cent of phosphoric acid, as in analysis of hydro-disodium-phosphate.

It is well after dissolving the precipitate of phospho-molybdate in ammonia, to let the solution stand for some hours, to allow the silica to separate from any silico-molybdate that may possibly be present, before adding the magnesium mixture. Should any silica be deposited, by the decomposition of silico-molybdate in the ammoniacal solution, filter it out, add the magnesium mixture, and proceed as above.

To determine the water, as some may remain after drying the limestone at 150° C., proceed as directed in the analysis of hydro-disodium phosphate, weighing it after absorption in calcium chloride.

To determine the organic matter the same method can be followed as that suggested for the determination of carbonic acid, in anhydrous carbonates, by fusion with borax. (See Fres., § 139—II.—c.) The loss of weight will be carbonic acid, water, and organic matter. The difference between this and the sum of the weights of carbonic acid and water previously determined will be the weight of organic matter. Of course, the fusion with borax must be carefully done, and the determination of carbonic acid and water be accurate, to give correct results.

Another method is, to dissolve 15 or 20 gms. of the limestone in dilute hydrochloric acid, heat it gently to expel carbonic acid, filter out any undissolved residue

through ignited asbestos, wash it well with water, dry it, transfer it, with the asbestos, to a platinum boat, introduce the boat into a combustion-tube of hard glass containing oxide of copper, and ignite it in a current of dry oxygen, absorbing the resulting carbonic acid, and from it calculating the carbon, 58 parts of which, according to Petzholdt, correspond to 100 parts of humus. (See *Jour. f. Prakt. Chem.*, LXIII., 194.)

To determine barium, strontium, and manganese, evaporate to dryness the filtrate from the residue used for the determination of organic matter, and heat in an air-bath at 100° C., until the odor of hydrochloric acid disappears. Then moisten with HCl and a drop of H₂SO₄, digest with hot water, filter, and wash. The residue will consist of silica, and perhaps baryta, and strontia in the form of sulphates; while the filtrate will contain the manganese, with other constituents of the limestone.

Expel the silica from the residue with ammonium fluoride and sulphuric acid, in the manner described in the analysis of feldspar. If any residue remain, fuse it with sodium carbonate, digest with hot water, filter, and wash well. Barium and strontium will remain on the filter as carbonates. Dissolve them through the filter with dilute hydrochloric acid, nearly neutralize the solution with ammonia, and add a few drops of sulphuric acid, and allow to stand for some hours. Should a precipitate of barium sulphate, and perhaps strontium sulphate form, filter it out and wash it, and allow the filtrate and washings to run into a small flask. Then stop the point of the funnel, fill the filter with a strong solution of ammonium carbonate, and allow it to stand for 12 hours. By this means, the strontium sulphate will be converted into carbonate, while the barium sulphate will be unattacked. Remove the plug from the point of the funnel, allow the fluid to run into the flask with the first filtrate, wash with hot water, and run dilute hydrochloric acid through the filter into the flask; the object of using

which is to prevent loss by effervescence by the contact of the acid with the solution of alkaline carbonate below. Finally, wash with water, dry the filter and contents, and determine the barium sulphate as usual.

To the combined filtrates in the flask add ammonia and ammonium carbonate, and if a precipitate of strontium carbonate forms, filter it through a very small filter, wash with dilute ammonia, dry, ignite, and weigh the strontium carbonate. Be careful to clean the filter well, and ignite it separately. (See Fres., §§ 72 and 102.)

To the first filtrate from the silica, baryta, and strontia add a few drops of nitric acid, boil, dilute, nearly neutralize with sodium carbonate, add excess of sodium acetate, boil and filter out the ferric hydrate, alumina and phosphoric acid, wash slightly, concentrate to small bulk, filter again if necessary, run the solution, rendered alkaline by a few drops of ammonia, into a small flask, nearly fill the flask, add freshly-prepared ammonium sulphide, cork the flask, and set it aside for 24 hours for the manganese sulphide to precipitate. When the manganese sulphide has entirely settled, decant off the clear fluid into a beaker, not on a filter, wash by decantation into a beaker 3 or 4 times, with water containing ammonium sulphide and a little ammonium chloride, and then on a filter with the same. Then transfer the moist precipitate to a small beaker, add hydrochloric acid, warm until the mixture smells no longer of hydrogen sulphide, dilute slightly, filter, and wash carefully. Then heat the fluid to boiling, remove the heat, add solution of sodium carbonate until the fluid is distinctly alkaline, boil until the carbonic acid is expelled, filter, wash with hot water until the washings are not alkaline to test-paper, dry, ignite, cool, and weigh the manganous-manganic oxide (Mn_2O_4), and calculate the manganous oxide (MnO).

To determine the chlorine, dissolve 40 or 50 gms. of the limestone in nitric acid, filter, if necessary, and determine the chlorine as directed in the analysis of barium chloride.

To determine the fluorine, dissolve 40 or 50 gms. of the limestone in acetic acid, filter, and in the residue determine the fluorine, by fusing and proceeding as directed in the analysis of calcium fluoride.

To determine the alkalies, dissolve about 20 gms. of the mineral in hydrochloric acid, add chlorine water and heat for a short time. Should there be any residue, filter it out and decompose it by J. Lawrence Smith's method, given in analysis of feldspar. Combine the filtrate, which may contain some alkali, with the main solution. Then add ammonia in slight excess, and ammonium carbonate, and allow the solution to stand for several hours; after this, filter, wash, evaporate the filtrate and washings to dryness, in a platinum dish, and expel the ammonia salts by igniting to a point just below redness. Dissolve in water, add solution of barium hydrate, until the fluid is decidedly alkaline, filter and wash well, and add to the filtrate solution of ammonium carbonate as long as it produces a precipitate, allow the fluid to stand for a short time, filter out the barium carbonate, and wash it until the washings do not render silver nitrate turbid. Then evaporate the filtrate in a weighed platinum dish, after adding a drop of hydrochloric acid, ignite to faint redness, cool, and weigh the mixed chlorides of the alkalies. It is well to dissolve in water, and repeat the treatment with barium hydrate and ammonium carbonate, and again evaporate and weigh. Separate the alkalies, and determine them as directed in analysis of feldspar.

NOTE.—Many limestones contain silica either in the form of quartz or as silicates undecomposable by acids when treated as described. In such cases the silica or silicates separate readily from the solution in a sandy form, whereas if a partially soluble silicate is present the insoluble portion will be flocculent to some extent. When, therefore, the insoluble portion is *all* sandy in character, it will be unnecessary to evaporate the main solution. Much time can then be saved by evaporating *only* the solution obtained upon fusion of the insoluble portion, filtering off SiO_2 , combining the filtrate with the main solution, and proceeding as described.

The lime may be determined volumetrically by the indirect method described (Chapter III., Calcium Carbonate).

CHAPTER XII.

CLAY.

Clay is derived principally from the decomposition of feldspar, or rather feldspathic rocks, and varies in composition and color, on account of varying quantities of feldspar sand (or feldspar reduced to a granular condition and not decomposed), quartz in the form of sand, lime, magnesia, oxide of iron, and manganese. Sometimes oxide of titanium and other minerals in small quantities are found.

The kinds of clay more commonly known are common brick clay, ordinary pottery clay, slate, fire-clay, and kaolin or porcelain clay. The difference between them is due less to the character of the constituents than to their relative quantity.

It is sometimes necessary to make a mechanical analysis by separation of the coarse from the fine parts. For description of methods, and of apparatus, consult *Jour. f. Prakt. Chem.*, XLVII., 241, and *Am. Jour. Sci. & Arts*, 3d series, VI., 288.

For the chemical analysis dry 20 or 30 gms. of the finely-pulverized clay at a temperature of 100° C. to constant weight, and keep the powder in a well-corked bottle.

The loss of weight in drying will be equivalent to the water.

Fuse 1 gm. of the dry powder with a mixture of equal parts by weight of sodium and potassium carbonates, and proceed exactly as directed in the analysis of feldspar, for the determination of silica, oxide of iron, alumina, lime, and magnesia.

After weighing the silica, expel it by Rose's method, with ammonium fluoride, and test any residue which remains qualitatively for titanium. Should any be

detected, fuse 5 gms. of the material with sodium fluoride and acid sodium sulphate, as directed in partial analysis of iron ore, bring into cold water solution, add excess of potassium hydrate, filter out the precipitated titanium dioxide, wash, dry, transfer the precipitate to a capacious platinum crucible, burn the filter and add the ash, and fuse all with 10 or 12 times the weight of acid sodium sulphate. Cool and digest with concentrated sulphuric acid. When the mass is cool, dissolve it in cold water, and precipitate the titanium dioxide by boiling. (Compare analysis of titaniferous iron ore.)

For the determination of manganese and other constituents, consult analysis of limestone.

Determine the alkalies as in analysis of feldspar.

To ascertain how much of the silica found exists in combination with the bases of the clay, how much as hydrated acid, and how much as quartz sand, or as a silicate present in the form of sand, proceed as follows. (Compare Fres. *Quant. Anal.*, 5th ed. 1865, § 236.)

Let *A* represent silica in combination with bases of the clay.

Let *B* represent hydrated silicic acid.

Let *C* represent quartz sand, and silicates in the form of sand, *e. g.*, feldspar sand.

Dry 2 gms. of the clay at a temperature of 100° C., heat with sulphuric acid, to which a little water has been added, for 8 or 10 hours, evaporate to dryness, cool, add water, filter out the undissolved residue, wash, dry, and weigh ($A+B+C$). Then treat it with sodium carbonate as directed by Rose, p. 923. Transfer it, in small portions at a time, to a boiling solution of sodium carbonate contained in a platinum dish, boil for some time, and filter off each time, still very hot. When all is transferred to the dish, boil repeatedly with strong solution of sodium carbonate, until a few drops of the fluid, finally passing through the filter, remain clear on warming with ammonium chloride. Wash the residue, first with hot water, then (to insure the

removal of every trace of sodium carbonate which may still adhere to it) with water slightly acidified with hydrochloric acid, and finally with water. This will dissolve ($A+B$), and leave a residue (C) of sand, which dry, ignite, and weigh.

To determine (B) boil 4 or 5 gms. of the clay (previously dried at 100° C.) directly with a strong solution of sodium carbonate, in a platinum dish as above, filter and wash thoroughly with hot water. Acidify the filtrate with hydrochloric acid, evaporate to dryness, and determine the silica as usual. It represents (B) or the hydrated silicic acid.

Add together the weights of (B) and (C), thus found, and subtract the sum from the weight of the first residue ($A+B+C$). The difference will be the weight of (A) or the silica in combination with bases of the clay.

If the weight of ($A+B+C$) found here be the same as that of the silica found by fusion in a similar quantity, in the analysis of the clay, the sand is quartz, but if the weight of ($A+B+C$) be greater, then the sand contains silicates.

The weight of the bases combined with silica to silicates can be found by subtracting the weight of total silica found in 1 gm. in the regular analysis, from the weight of ($A+B+C$) in 1 gm.

CHAPTER XIII.

MANGANESE ORE.

The plan to be pursued for the determination of the manganese may be sketched thus :

Dissolve 1 gm. in 5 c. c. conc. HCl, dilute and filter.

Residue A. Test for Mn by blow- pipe.	Solution A. Cool, neutralize with Na_2CO_3 , add 0.5 gm. $\text{NaC}_2\text{H}_3\text{O}_2$, boil. (Basic acetate separation.) Filter.	
	Precipitate B. Fe_2O_3 , Al_2O_3 , P_2O_5 , etc. Dissolve in HCl. Repeat basic acetate separation as often as may be necessary. Add filtrates to Solu- tion B.	Solution B. Add 5 gms. $\text{NaC}_2\text{H}_3\text{O}_2$ and 2 to 3 c. c. Br. Boil till colorless.
		Precipitate C. $\text{MnO}_2 \cdot x\text{H}_2\text{O}$. Dissolve in $\text{HCl} + \text{SO}_2$. Boil, add solution of $\text{NaNH}_4\text{HPO}_4$, neutralize with ammonia, heat until crystalline, filter, wash, ignite, and weigh $\text{Mn}_2\text{P}_2\text{O}_7$.

Solution C.
 Ca , Mg , etc.
Reject.

In dissolving the ore, which usually contains much MnO_2 , a small vessel is most convenient. On adding the strong hydrochloric acid, the attack usually begins at once in the cold, and if a casserole or beaker is used it should be at once covered to avoid loss by spattering. After the first action is over, the vessel may be heated up gradually to boiling. The addition of a little more strong hydrochloric acid may in some cases be necessary.

With many ores the insoluble portion consists of light-colored silica, but sometimes dark-colored minerals may be present, not readily decomposed by the acid, though containing no manganese. In any case, test the insoluble residue by fusion with alkaline carbonate, with addition of a little nitrate. If the mass on cooling is white or has only a slight greenish-blue tinge, it may be rejected. If, however, it is quite green, it should be dissolved in hydrochloric acid, the solution evaporated to dryness, as in the

limestone analysis, and the filtrate from the silica added to the main solution.

In solution A the neutralization with sodium carbonate is carried to the point at which the solution assumes a deep reddish-brown tint, but is free from any precipitate (in the cold). The tint obtained is due to the iron which is almost invariably present. If it should happen, however, that iron is small in amount or absent, the addition of sodium carbonate should be stopped just before it reaches the point where it produces a precipitate not removable by vigorous stirring and then standing for two or three minutes. If this point has been passed, add two drops of hydrochloric acid, stir well and allow it to stand for two or three minutes. If it does not then clear, repeat the addition of acid and stirring until it does. The proportion of sodium acetate then to be added should be restricted. The larger the amount added beyond a certain point, the larger the amount of manganese in the precipitate.*

A second precipitation is usually necessary when the ore contains 30 per cent or more of manganese, and a third or possibly even a fourth may prove desirable. Careful blowpipe tests on portions of the precipitate will show.

If the bulk of the combined filtrates much exceeds 200 to 300 c. c. it should be concentrated by evaporation. During evaporation some blackish-brown manganese dioxide may separate. If the precipitate which separates in this manner shows no reddish tinge of iron, it may be disregarded; and if it adheres to the sides of the casserole, it may be dissolved in the mixture intended for the solution of the precipitate from the bromine treatment. If, however, it contains iron, it must be filtered off, dissolved in hydrochloric acid, the iron precipitated as basic acetate, and the solution united with the main one.

In solution B the presence of an *excess* of sodium acetate is necessary to facilitate the separation of the manga-

* If one uses a solution of sodium acetate saturated at ordinary temperatures, it may be assumed that 3 c. c. contains about 1 gm. of the salt.

nese as dioxide. The use of liquid bromine, instead of its solution in water, is preferable to avoid unnecessary dilution. Enough bromine must be used to show a yellow tint in the *clear* liquid while it is at a boiling heat. It is well to add a little more bromine to the filtrate, and to boil again, to be sure that the manganese is completely precipitated.

The precipitated manganese dioxide (precipitate C) can be dissolved in strong hydrochloric acid, but the strength of acid required for ready solution is such that the filter-paper may be attacked, which is objectionable. In the presence of a reducing agent, as sulphurous acid, (either added as such or in the form of some alkaline sulphite or bisulphite,) the precipitate dissolves easily in dilute hydrochloric acid. It is best to transfer as much of the precipitate as possible from the filter to the beaker in which the precipitation was made, and then, placing this beaker under the funnel, to pour through the filter the hot solution of dilute hydrochloric acid containing sulphurous acid.

The phosphate separation of manganese is now usually preferred. Formerly it was the custom to precipitate as carbonate. For this the hydrochloric solution of the precipitate is brought to boiling, and enough sodium carbonate solution added to render it alkaline. Then, after boiling for a short time, the precipitate is washed several times by decantation. Prolonged washing is necessary, as it is very difficult to remove the last portions of alkali from the precipitate. After thorough washing the precipitate is dried and ignited with access of air to black Mn_2O_3 , before weighing.

In the phosphate separation the precipitate obtained is $MnNH_4PO_4$, similar in constitution to the magnesium precipitate, but managed in a different manner. The reagent ("salt of phosphorus" or "microcosmic salt") must be added in decided excess to the *acid* solution containing the manganese, and the mixture heated for a short

time before neutralization. About three times as much of the reagent as will suffice to combine with the manganese must be added* to render the precipitate sufficiently insoluble.

Then bring the solution to a boil, and add ammonia gradually until the solution just smells of that reagent after stirring. Place the beaker on the boiling-water-bath, and allow it to stand thus hot until the precipitate has become *completely crystalline* and settles readily. The precipitate should be white or nearly so, with possibly a faint tinge of pink. If it looks brownish, too much ammonia is present, and it should be redissolved by addition of hydrochloric acid, and reprecipitated by cautious addition of ammonia. Filter, wash with hot water, dry and ignite, raising the heat gradually at first, finally applying the full heat of the burner. From the weight of $Mn_2P_2O_8$, calculate percentage of Mn.

The chlorate separation of manganese is preferred by some. This depends on the fact that the addition of crystals of potassium chlorate to a solution of manganese in strong nitric acid precipitates MnO_2 on boiling. If iron is present, a small amount precipitates with the manganese. Hydrochloric acid or chlorides should not be present in the solution. The process known as the Ford or Ford-Williams method (*Trans. Am. Inst. Min. Eng.*, IX., 397, and X., 100) is frequently used in the analysis of spiegel, ferro-manganese, etc. for which it was originally proposed. Applied to a mineral it is as follows:

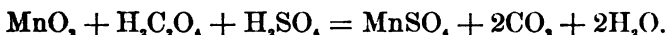
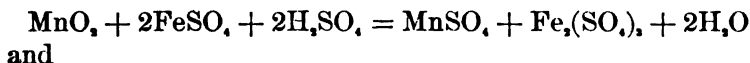
Treat 0.5 gm. of ore with 5 c. c. concent. hydrochloric acid. Warm gently, and then add 10 c. c. of water, and boil down to very small bulk. Then add 25 to 30 c. c. of strong nitric acid, and boil down again to expel hydrochloric acid. Now add 75 c. c. strong nitric acid, and apply

* A solution of microcosmic salt saturated at ordinary temperatures will contain about 0.17 gm. per c. c. 15 c. c. will just about suffice to react with the manganese in 1 gm. of MnO_2 . About 40 c. c. of the saturated solution will therefore be the proper amount if 1 gm. of the ore was taken.

heat. When the solution is warm add 3 or 4 gms. of potassium chlorate crystals, bring the solution to a boil, and continue boiling for about ten minutes (when the fumes escaping should be free from all color and odor of chlorine). Allow it to cool somewhat, add about 3 gms. more of chlorate crystals, and boil again for about ten minutes. The casserole or beaker in which this operation is conducted should be sufficiently capacious to avoid danger of frothing over during the first part of the boiling. Cool the solution, and filter through asbestos.* Wash two or three times with strong nitric acid,† and then with water.

From this point one may follow Ford's original plan or Williams's modification. According to the former the precipitate is dissolved in hydrochloric and sulphurous acids, the iron separated as basic acetate (in the manner already described), and in the filtrate the manganese is precipitated and determined as phosphate.

Williams's method consists in determining the oxidizing power of the MnO_2 in the precipitate by the use of either ferrous sulphate or oxalic acid, in conjunction with sulphuric. The reactions are respectively



A description of the process with oxalic acid will suffice, the two being similar in all respects.

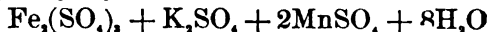
The precipitate (asbestos and all) is treated in the vessel in which the precipitation was made, with 100 of water, 10 c. c. concentrated sulphuric acid, and (50 c. c. to

* The asbestos used should be previously tested in blank, to see that it gives up no substances which will cause interference (lime or magnesia in the Ford method—gravimetric; ferrous iron or other reducing material in the Ford-Williams method—volumetric).

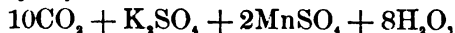
† Nitric acid which has been exposed to light contains nitrous acid and lower nitrogen oxides, which will dissolve some MnO_2 at this stage, and therefore such should be removed by blowing a current of air through the acid if it has the faintest yellow tint.

100 c. c.) a measured amount of a solution containing 11.45 gms. crystallized oxalic acid per litre. (1 c. c. = about 0.005 gm. Mn). The mixture is heated to effect solution of the precipitate, and meantime a convenient amount (20 c. c.) of the original oxalic-acid solution may be titrated with standard permanganate. When the precipitate of MnO_2 is dissolved that solution may also be titrated in the same way (at 60°C.). From the data thus obtained the oxidizing power of the precipitate or, *per contra*, the amount of Mn in it may be found.

To calculate the value of the permanganate solution for this titration we need only to compare the relative oxidizing power of $\text{K}_2\text{Mn}_2\text{O}_8$ and of MnO_2 . Since the permanganate is usually standardized for Fe, it will also be convenient to determine the relation of its values for Fe and for Mn. Comparing the above equations with those for the action of permanganate, which are



and



we see that MnO_2 has only one fifth as much oxidizing power as $\text{K}_2\text{Mn}_2\text{O}_8$, molecule for molecule, or that 316 parts of $\text{K}_2\text{Mn}_2\text{O}_8$ have the oxidizing power of ($5 \times 55 =$) 275 parts of manganese when in the form of MnO_2 . For a solution containing 3.16 gms. $\text{K}_2\text{Mn}_2\text{O}_8$ per litre 1 c. c. would equal 0.00275 gm. Mn as MnO_2 . It must not be forgotten that the calculation is in a certain sense reversed, being based on the amount of *permanganate rendered unnecessary* by the oxidizing power of the precipitated MnO_2 .

From the first one of the last pair of equations we see that for a solution containing 3.16 gms. $\text{K}_2\text{Mn}_2\text{O}_8$ per litre 1 c. c. = 0.0056 gm. Fe. Hence

$$\text{Fe standard: Mn standard} = 0.0056 : 0.00275 = 1 : 0.49107,$$

or

$$\text{Fe standard} \times 0.49107 = \text{Mn standard}.$$

The Volhard method of determining manganese depends

on the fact that in a neutral solution containing only sulphates or nitrates and a manganous salt, the addition of permanganate determines the precipitation of MnO_2 , a redistribution of the oxygen combined with the manganese in its two forms (manganous and permanganic) taking place thus: $\text{Mn}_2\text{O}_3 + 3\text{MnO} = 5\text{MnO}_2$. The solution is rendered neutral by the use of zinc oxide.*

The operation is conducted as follows: Decompose 1 gm. of the mineral with 5 c. c. of concentrated hydrochloric acid, applying heat until complete decomposition is effected. Then add about 30 c. c. of water and 5 to 10 c. c. of concentrated sulphuric acid and evaporate to fumes of SO_3 . Cool, dilute to 100 c. c., and heat to dissolve the metallic sulphates. At this point if there is any doubt as to the decomposition of the mineral, filter off and test the insoluble residue for manganese. If not, the filtration may be omitted. Nearly neutralize with sodium carbonate, and then pour in slowly with stirring a cream of zinc oxide (or hydrate) suspended in water. When enough has been added, the precipitate coagulates and settles readily. Cool the solution if it is not already at the temperature of the laboratory, dilute to one litre, mix well, and allow it to stand and settle. A slight cloud of zinc oxide may remain in suspension, but so long as the suspended material contains no perceptible tinge of iron it is of no importance. Draw off lots of 100 c. c. each of the supernatant solution into casseroles, dilute each with about 100 c. c. of hot water, and heat nearly to boiling. Titrate one after the other with standard permanganate solution. The solutions should be hot, but should never be boiled after commencing the titration. Stir vigorously while adding the permanganate and for a few seconds after, and then allow

* Commercial zinc white frequently contains small amounts of manganese. It is purified by adding an excess of the oxide to HCl , precipitating out what manganese may be present by addition of bromine, filtering, and from the clear solution precipitating the zinc by addition of ammonia, carefully avoiding any excess. After filtering and thorough washing it is ready for use.

the precipitate to settle. The titration is finished when the supernatant liquid shows a faint tinge of pink against the white of the casserole. If the permanganate is added slowly, a brown deposit of MnO_2 forms on the sides of the casserole, rendering it difficult to see the end reaction. It is therefore better to use the first lot of 100 c. c. to get an approximate result, adding 1 c. c. at a time toward the last, and using the succeeding lots of 100 c. c. to get more exact results.

To calculate the standard of the permanganate solution. Referring to equation given, and remembering that Mn_2O_3 represents the manganese oxide in $K_2Mn_2O_7$, a course of reasoning similar to that pursued in the previous discussion would lead to the conclusion that for a solution containing 3.16 gms. $K_2Mn_2O_7$ per litre, 1 c. c. would equal 0.00165 Mn. ($3 \times 55 = 165$), and

Fe standard : Mn standard = $0.0056 : 0.00165 = 1 : 0.29464$
or Fe standard $\times 0.2964 =$ Mn standard.

The commercial value of manganese ore depends chiefly upon the quantity of chlorine it will yield when treated with hydrochloric acid.

By available oxygen is meant the excess of oxygen over the 1 atom combined with manganese to form monoxide, and, as only half of the oxygen of manganese dioxide is available, 16 parts of oxygen are equivalent to 87 parts of manganese dioxide, and, as in the decomposition of 1 molecule of manganese dioxide by hydrochloric acid 2 atoms of chlorine are liberated, 16 parts of oxygen are also equivalent to 71 parts of chlorine.

To determine the available oxygen, introduce into flask "B" of the apparatus described in the analysis of calcite, about 3 gms. of the ore, very finely pulverized, and carefully dried at $100^\circ C$. The best method of determining the quantity of ore taken is that described in the analysis of potash alum, by weighing a tube containing pulverized and dried ore, shaking out the desired quantity, again weighing the tube and determining the weight of ore

taken by the loss. Introduce also into the flask about 7 or 8 gms. of neutral potassium oxalate, and as much water as will fill it to about one quarter. Fill flasks "A" and "C" of the apparatus about one quarter full of pure concentrated sulphuric acid. Put the apparatus together, weigh it, and proceed as directed in the analysis of calcium carbonate, for the determination of carbonic acid by loss, drawing about 1 litre of air through the flasks, very slowly, by means of an aspirator, not allowing air-bubbles to pass faster than 2 per second. The heat generated by the union of the water and sulphuric acid is sufficient. The difference in the weight of the apparatus, before and after the operation, is equivalent to the weight of carbonic acid lost. (Fres., § 230.)

The method of calculating the available oxygen is evident upon an examination of the equation representing the reaction :



Two molecules of carbonic acid are equivalent to one molecule of manganese dioxide, *i. e.*, 88 parts by weight of carbonic acid represent 87 parts by weight of manganese dioxide. Therefore, if the weight of carbonic acid is multiplied by 87, and the product divided by 88, the quotient will be the weight of manganese dioxide. As only one half of the oxygen of manganese dioxide is available, it is calculated by a simple proportion, *viz.*, $87 : 16 = \text{weight of MnO}_2 ; \text{weight of available O}.$

Some ores of manganese contain carbonates, the carbonic acid of which must, of course, be removed before the analysis is made. If such be the case, introduce the ore as before into flask "B," fill it about one quarter full with water, add dilute sulphuric acid (1 part acid to 5 parts water), little by little, until effervescence ceases, and the fluid remains acid after boiling out the carbonic acid. Then neutralize the excess of acid with sodium or potassium hydrate, free from carbonic acid, add the usual

quantity of neutral oxalate, and proceed as before. (*Zeitschrift f. Analyt. Chem.*, 1, 48.)

Another method is that known as the iron method. Fresenius's directions are to dissolve in a long-necked flask, placed in a slanting position, 1 gm. of piano-forte wire, using in this case pure concentrated hydrochloric acid; then weigh about 0.600 gm. of the ore, in a little tube, drop this with its contents into the flask, and heat cautiously until the ore is dissolved. One eq. of manganese dioxide, or 87 parts, converts 2 eqs. of iron, or 112 parts, from the state of ferrous to that of ferric chloride. When complete solution has taken place, dilute the contents of the flask with water, allow to cool, rinse into a beaker, and determine the iron still remaining in the state of ferrous chloride with potassium bichromate. (See analysis of ammonio ferric sulphate.) Deduct this from the weight of the wire employed in the process. The difference expresses the quantity of iron, which has been converted by the oxygen of the manganese from ferrous to ferric chloride. This difference, multiplied by 87, and divided by 112, gives the amount of manganese dioxide in the ore.

Pattinson has suggested a modification of this method, in a paper read before the Newcastle-upon-Tyne Chem. Soc., Jan. 27, 1870. His test analyses are very satisfactory. He directs to dissolve about 2 gms. of clean iron wire in a flask holding about 500 c. c., with about 90 c. c. of dilute sulphuric acid, made by adding 3 parts of water to 1 part of the acid. A cork, through which passes a tube bent twice at right angles, is inserted in the neck of the flask, and the flask is heated over a gas flame until the iron is dissolved. The bent tube is placed so as to dip into a small flask or beaker containing a little water. When the iron is quite dissolved, 2 gms. of the finely pounded and dried sample of manganese ore to be tested are put into the flask, the cork replaced, and the contents again made to boil gently over a gas flame, until it is seen

that the whole of the black part of the sample is dissolved. The water in the small flask or beaker is then allowed to recede through the bent tube into the larger flask, more distilled water is added to rinse out the small flask or beaker and bent tube, the cork well rinsed, and the contents of the flask made up to about 250 or 300 c. c. with distilled water. The amount of iron remaining unoxidized in the solution is then ascertained by means of a standard solution of potassium bichromate. The amount the bichromate indicates, deducted from the total amount of iron used, gives the amount of iron which has been oxidized to the ferric form by the manganese ore, and from which can be calculated the percentage of peroxide of manganese contained in the ore. Thus, supposing that 0.250 gm. of iron remained unoxidized, then if 2 gms. of iron were taken at first, 1.750 gms. of iron will have been oxidized by the ore. Then as

$$112 : 87 = 1.750 : 1.359 \text{ gm. MnO}_2,$$

which, if 2 gms. of ore were taken for the test, would represent 67.95 per cent of MnO_2 in the ore.

Standardized solution of potassium permanganate can be used instead of bichromate.

It is frequently of importance to know the amount of hydrochloric acid necessary to decompose an ore of manganese. This can be determined with sufficient accuracy for commercial purposes, by what is called Kiefer's solution, (*Ann. d. Chem. u. Pharm.*, XCIII., 386.)

To prepare the solution, dissolve 15 gms. recrystallized copper sulphate in 100 c. c. of warm water, and add ammonia, with stirring, until the basic salt is *nearly dissolved*. Should the point be overstepped, add more copper sulphate, and repeat. Filter the solution, and add the filtrate from a burette, with constant stirring, to 10 c. c. of half-normal sulphuric acid, until a permanent turbidity is produced, and note the number of c. c. used. As 10 c. c. of half-normal sulphuric acid is equivalent to 0.365 gm. of hydrochloric acid, this, divided by the number of c. c. of

the copper sulphate solution used, shows the quantity of hydrochloric acid represented by 1 c. c. of it. This is standard copper sulphate solution.

The next step is to prepare a solution of hydrochloric acid of 1.1 sp. gr., and to 10 c. c. of it add the standard copper sulphate solution, drop by drop, with constant stirring, until the fluid becomes slightly turbid. The number of c. c. of copper sulphate solution used multiplied by the previously ascertained value of 1 c. c. of it, gives the quantity of hydrochloric acid in the hydrochloric acid solution of 1.1 sp. gr.

Then, into a flask, through the cork of which passes a tube about 3 feet long, and of about one quarter of an inch diameter, and bent slightly from the perpendicular, introduce 1 gm. of the manganese ore to be tested and 10 c. c. of the standardized hydrochloric acid, and heat gently until the ore is decomposed, and then more strongly for a few minutes until the chlorine is expelled.

The object of the long tube is to condense the vapor, and allow the fluid to run back into the flask. To insure this, it is well to wrap it with a wet cloth and keep it cool.

After the chlorine is expelled, cool the flask, add 25 c. c. of cold water, filter, and wash with 25 or 30 c. c. of cold water. Then to the filtrate add, as before, standard copper sulphate solution, until the fluid is slightly turbid. The number of c. c. used shows the quantity of free hydrochloric acid present.

The difference between the quantity of hydrochloric acid found in 10 c. c. of the solution of 1.1 sp. gr. before adding it to the ore, and the quantity in 10 c. c. after using it for dissolving the ore, gives the quantity required to dissolve 1 gm. of the ore.

The calculation of the manganese oxides in an ore is best illustrated by an example :

Suppose total Mn = 25.24 per cent and available O = 6 per cent.

Calculate first the available oxygen to make MnO_2 ,

$$(\text{O}) 16 : (\text{MnO}_2) 87 = 6 : 34.62.$$

Calculate the Mn corresponding to this :

$$(\text{MnO}_2) 87 : (\text{Mn}) 55 = 32.62 : 20.62.$$

Total Mn as above..... 25.24

Mn as MnO_2 , calculated above..... 20.62

Difference..... 4.62 per cent Mn

Calculate this as MnO . It is equivalent to 5.96 per cent, since

$$(\text{Mn}) 55 : (\text{MnO}) 71 = 4.62 : 5.96.$$

Calculate MnO_2 required to combine with this to form Mn_2O_3 :

$$(\text{MnO}) 71 : (\text{MnO}_2) 87 = 5.96 : 7.80. \quad \text{MnO} + \text{MnO}_2 = \text{Mn}_2\text{O}_3.$$

Mn_2O_3 , then, is $(\text{MnO} = 5.96) + (\text{MnO}_2 = 7.80) = 13.26$ per cent Mn_2O_3 .

Total MnO_2 calculated from available O = 32.62

Deduct MnO_2 combining to form $\text{Mn}_2\text{O}_3 = 7.80$

Difference = MnO_2 existing as such..... 25.82

Or the ore contains

Mn_2O_3 13.26 per cent.

MnO_2 25.82 per cent.

CHAPTER XIV.

PARTIAL ANALYSIS OF IRON ORES.

The ordinary constituents of iron ores are iron oxides, phosphorus (as phosphate), sulphur (usually as sulphide), silica (as quartz or in combination), alumina, lime, and magnesia; manganese is usually, though not invariably, present. Besides these water (as moisture or in combination), carbon dioxide, and titanous acid are of frequent occurrence, and more infrequently arsenic, copper, zinc, barium, nickel, cobalt, etc., more rarely chlorine, fluorine, vanadium, tungsten, and other rare elements.

In many cases, the determination of iron, phosphorus, sulphur, and silica is sufficient for the purposes of the iron-master. In such cases, where arsenic, barium, and titanium are absent the plan of analysis in brief would be as follows:

- a. Fuse 5 gms. with 25 gms. NaKCO_3 , and a little alkaline nitrate.
- b. Dissolve in dilute HCl and evaporate to dryness. Take up with dilute HCl and filter.
- c. Residue = SiO_2 . Solution c. Divide according to requirements.

d = $\frac{1}{2}$ c. Precipitate with ammonia and filter, dissolve precipitate in H_2SO_4 , reduce with Zn and titrate.

Filtrate d. Acidify with HCl , and precipitate SO_3 by BaCl_2 .

e. $\frac{1}{2}$ c, or $\frac{1}{3}$ and $\frac{1}{3}$ c done in duplicate. Precipitate e by ammonia (or basic acetate). Dissolve ppt. in HNO_3 , evaporate low, dilute, precipitate the solution with $(\text{NH}_4)_2\text{MoO}_4$ reagent; dissolve ppt. in ammonia, add "magnesia mixture," filter off MgNH_4PO_4 , ignite, and weigh $\text{Mg}_3\text{P}_2\text{O}_8$ for P.

Filtrate e from ammonia may be used for S det'n. If from basic acetate, may be used for determining Mn, Ca, and Mg, one or all.

Whatever the method used for the decomposition of the ore, the portion taken for analysis should be finely pulverized in an agate mortar until the powder feels soft when rubbed between the fingers.

a. *Decomposing the Ore.*—Boiling concentrated hydro-

chloric acid will decompose some iron ores completely. If, however, the sulphur is to be determined, some nitric acid must also be used, to convert the sulphur (usually present as sulphide) into sulphate. In most cases it is more advantageous to decompose the ore by fusion with about five times its weight of alkaline carbonates, and treating with hydrochloric acid.

A mixture of dry sodium and potassium carbonates in the proportion of their molecular weights (106 to 138), or a fairly close approximation thereto (11 to 14), fuses at a lower temperature than either alone, and constitutes an excellent flux for this purpose. The amount of alkaline nitrate (either the sodium or potassium salt) to be used depends upon the proportion of sulphur present. Its use is chiefly to convert the sulphur of the sulphides into sulphate, although it serves a subordinate purpose in converting any ferrous iron which may be present completely into the ferric form. 1 to 1.5 gms. usually suffice (preferably the smaller quantity) unless a qualitative test on the ore indicates that much sulphide is present. The larger the amount of nitrate used unnecessarily, the greater the danger of attacking the platinum of the crucible, since, though dilution by the carbonate modifies, it does not entirely prevent such attack. This is disadvantageous, both for the "life" of the crucible, and from the presence of platinum salts in the analysis.

To weigh out the materials it will be found convenient to counterpoise, on the balance, a clean and dry platinum crucible of suitable capacity (40 to 60 c. c.) and then to weigh directly in that the necessary amount of the pulverized ore, the amount to be taken depending to some extent upon the proportion of phosphorus supposed to be present, or upon the plan of proceeding proposed (duplication of determinations, etc.). After weighing out the ore, the required proportions of carbonates and of nitrate, all in pulverulent form and dry, can be added directly on the ore in the crucible, weighing each constituent of the flux to

within 0.1 to 0.2 grm. Then, by means of a (dry) glass rod or stout platinum wire, mix the material in the crucible by stirring, until the color of the mass shows that it is fairly uniform. Settle the material well into the crucible by tapping and shaking, brush any adhering dust from the stirrer into the crucible by means of a feather, adjust the cover, and place the crucible on a platinum triangle well secured to the ring of a ring-stand. Then apply the full heat of a good Bunsen burner.

Fusion.—If the ore is very siliceous, a lively evolution of carbon dioxide may occur at first, in consequence of the reaction between the silica and the carbonates of the flux. The operation therefore needs watching at this stage, and it may be necessary to moderate the heat, either by temporarily removing the crucible-lid, or by lowering the flame, or both, lest the contents of the crucible boil over. When illuminating-gas is used for heating, removing the lid, or otherwise exposing the melt to the influences of the flame, may permit the introduction of sulphur from the gas into the analysis. Usually in a short time the effervescence ceases to be of a character to endanger the operation, and the full heat of the burner may be applied. No rule can be given for the length of time the mass should be kept in a state of fusion. Ordinarily between one and two hours are ample. The degree of subdivision and the character of the ore have an important bearing. Ores containing much alumina are usually especially refractory. In general it may be stated that the more difficult one finds it to pulverize the ore, the longer the fusion necessary for complete decomposition.

For some purposes, fusion with acid sulphates (potassium or sodium bisulphates) may be convenient. The flux should contain practically no water (hygroscopic or other), because if used moist it is liable to froth, perhaps even to boil over on heating. From ten to fifteen times as much flux as ore must be used, and the charge, mixed so far as possible, must be heated slowly up to red heat, at which

point it will remain quite liquid, with some evolution of sulphuric-acid fumes, though these should not be exceedingly copious. Toward the end of the operation, it is advisable to add to the crucible a few drops of concentrated sulphuric acid.

In the course of half an hour to an hour (perhaps more with very refractory ores) the heat may be withdrawn, and the mass allowed to cool. After cooling, dissolve in water. The insoluble residue consists principally, though seldom entirely, of silica, which is insoluble in the fused bisulphate. If the insoluble residue contains dark particles of undecomposed ore, a second fusion will be necessary.

With ores containing chromite Dittmar's flux may be used with advantage. This consists of a mixture of 3 parts of sodium and potassium carbonates with 2 parts of borax glass. These materials are mixed together, fused for a short time, and the mass broken up for use. The mode of managing with this flux will be more fully described under Analysis of Chromite.

Whatever flux may be used, the removal of the mass from the crucible in order that it may be treated with solvents is important. One method, generally applicable, consists in immersing in the melt, while still fluid, a bent platinum wire, and, after thorough cooling, applying the heat so as to soften the portion next to the crucible, and thus allow the mass to be lifted out. With the carbonate flux, if the melt is allowed to cool slowly and completely, it usually contracts so as to be easily separated by inverting the crucible and tapping it smartly. This method is especially successful when the interior of the crucible is smooth.

b. Dissolving the Melt.—If concentrated hydrochloric acid is poured upon the mass, the effervescence of carbon dioxide is less vigorous after the first moment than when diluted acid is used, because the alkaline chlorides which form are fairly insoluble in the strong acid, and check the action, even stopping it after a short time. The action

may accordingly be regulated by the cautious addition of water whenever the action slackens, care being exercised not to add too much water at a time, and thus incur danger of mechanical loss.

The solution should be made in a casserole, which is convenient for the subsequent evaporation. For a melt of 5 gms. ore and 25 gms. flux, 30 to 50 c. c. of concentrated hydrochloric acid will suffice for rinsing out the crucible and dissolving. As regards the amount of dilution, it must be remembered that on the one hand every drop added has to be evaporated off again, and on the other hand the more dilute the solution is made, the more free the resulting insoluble silica is from impurities (as alumina) after evaporation. The bulk had best be made up to 300 to 500 c. c. Some undissolved gelatinous silica may appear in the solution, and in the case of very siliceous ores this gelatinous silica may protect some lumps of the melt from complete solution. In that case it will be necessary to rub the gelatinous silica from the exterior of the lumps with a glass rod in order that the acid may penetrate them. Occasionally some dark particles of undecomposed ore may be seen, but if the ore was well pulverized they usually go into solution as the acid concentrates by evaporation.

The evaporation should be conducted on a sand-bath or iron plate, the heat being such as to keep the solution nearly boiling until the salts begin to crystallize out, when the casserole should be placed on a boiling-water-bath, and after that stirred from time to time in order to granulate the material so far as possible. When it becomes nearly dry (the lumps not adhering to one another) place the casserole in an air-bath kept at 120° C., and heat until no odor of acid is perceptible. Then cool, moisten with about 10 c. c. of concentrated hydrochloric acid, and heat on the water-bath for 10 or 15 minutes to dissolve the basic salts of iron and alumina. Then add enough hot water to dissolve the soluble salts, and filter, washing the silica

until a few drops of the washings cause no turbidity with silver nitrate.

c. *Insoluble Residue*.—The insoluble residue should be pure silica. It may, however, contain undecomposed ore, and possibly alumina, if much is present. In any case it should be ignited strongly and weighed. On igniting, especial care must be taken to char the paper *without flame*, since the silica is so extremely light that the flame would cause appreciable amounts to be lost. When the paper is completely carbonized and ceases to smoke, and *not until then*, it is safe to apply the full heat of the burner.

After igniting until it is perfectly white, it may be weighed as soon as cool without appreciable error, but if allowed to stand for some hours, exposed to the influence of the air, it will absorb some moisture. If it contains dark grains of undecomposed ore, or for any other reason it is suspected that it is not all pure silica, the silica should be driven off by means of hydrofluoric acid. Either hydrofluoric acid or ammonium fluoride may be added, in either case with addition of sulphuric acid to avoid loss of volatile fluorides other than silicon fluoride. A blank test should be made beforehand with the reagents, to determine the amount and character of the impurities, if any exist. The ammonium fluoride is more liable to contain impurities than the hydrofluoric acid at present obtainable for laboratory uses. If ammonium fluoride be used, the amount to be taken should be approximately calculated. Each molecule of SiO_2 (60 parts) requires 4 molecules (128 parts) of NH_4F . Allowing for moisture in the salt, etc., nearly three times as much ammonium fluoride as there is silica should be necessary. The amount of (concentrated) sulphuric acid to be used must be estimated in a similar manner. It should be added cautiously, drop by drop, or the effervescence may be too violent. If hydrofluoric acid is to be used, moisten the silica with a little water, and then add the acid, a little at a time, stirring with a plati-

num wire until the solution clears up. Then add a little concentrated sulphuric acid. Great caution is necessary to avoid contact of hydrofluoric acid with the skin of the hands or face, as it will produce painful sores which heal with difficulty. After addition of the reagents (with either method) place the crucible on a sand-bath or hot plate, and keep the temperature as high as possible without boiling. When all that can be driven off by this means is expelled, ignite on a platinum triangle by naked heat, beginning cautiously, and terminating with the strongest heat obtainable. It is always preferable to weigh, and then to repeat the treatment (with a small amount of fluoride) to insure removal of all the silica (shown by ceasing to lose weight). The weight of the silica is thus determined by loss, and the remainder, if any, is rendered soluble by a short fusion with alkaline carbonate, and the solution therefrom added to the main solution.

Solution c.—The filtrate and washings from the silica, to which perhaps may have been added the solution obtained as just described, is to serve for the determination of iron, phosphorus, sulphur, and perhaps other constituents of the ore. For the iron it is not desirable to use an amount of solution corresponding to more than 1 gm. For phosphorus and sulphur (and possibly others) the amount to be taken must be regulated by the indications afforded by qualitative tests on the ore. If they are large, 1 or 2 gms. may be sufficient, and one has an opportunity to carry through a duplicate determination, or to have a reserve portion in case of accident. If they are small, the solution representing 4 gms. may perhaps be used without division. In some cases it may seem advisable to use more ore than 5 gms. at the start, to provide for small percentages of phosphorus or of sulphur. 7 gms. of ore can be decomposed by the use of 25 gms. of flux as readily as 5 gms.

d. Determination of the Iron.—The method to be pursued consists in precipitating the ferric hydrate with

ammonia, dissolving that in acid, reducing to the ferrous form, and titrating. For precipitating with ammonia, heat the solution to boiling, and add rather rapidly enough ammonia to render the solution decidedly ammoniacal, stirring it all the time. An excess of the ammonia does not tend to redissolve the ferric hydrate, as in the case of alumina, and it is a matter of indifference whether some of the alumina goes into solution or not. If the ammonia is added gradually, the tendency is to precipitate some basic ferric sulphate along with the hydrate, and in this way a determination of sulphur in the filtrate (*d*) is rendered incorrect. After boiling for a few seconds, the solution is filtered hot, and washed with hot water until the washings give no cloud with barium chloride and a few drops of hydrochloric acid. Then by means of a spatula remove most of the precipitate from the filter, placing it in the beaker in which the precipitation was made. The acid to be used for dissolving the precipitate must be chosen with reference to the mode of titration proposed. If the permanganate titration, use sulphuric acid, and reduce with zinc; if the dichromate titration, use hydrochloric acid, and reduce with stannous chloride. Dilute the acid selected with six or eight times its bulk of water, heat the dilution, and then pour it through the filter, allowing it to run into the beaker containing the main bulk of the precipitate, and repeat this treatment until the filter-paper will remain perfectly white, even when a drop of ammonia is allowed to fall upon it. Then by stirring and warming—possibly by further addition of acid—bring the whole of the precipitate completely into solution. It is then in condition for reduction and titration, according to the methods already described under Iron Alum (Chapter IX.).

Filtrate d. Determination of Sulphur.—If the proportion of sulphur in the ore is apparently about 0.5 per cent or over, the filtrate from the ferric hydrate can be used for its determination. If apparently less, some or all of the solution obtained under *e* must be used, as will

be shown later. The solution contains the sulphur as sulphate, besides some alkaline chlorides and free ammonia. Since the presence of ammonia salts presents some inconveniences, on account of the tendency to hold finely divided barium sulphate in suspension, it will be best to boil out all or nearly all of the free ammonia before acidifying with hydrochloric acid. Afterward add to the hot solution (which should be filtered if not perfectly clear) 5 or 10 c. c. of the barium chloride solution, which should be boiled for a minute or two before adding; stir in well, and heat on the water-bath until the precipitate settles out, leaving the solution clear. Filter and wash with the precautions given in the analyses of barium chloride and magnesium sulphate (Chapters I. and II.). For the method of separating barium sulphate in solutions containing iron, see, later on in this chapter, separate determination of sulphur.

e. In the solution representing 4 gms. of the ore, divided or not, according to requirements, the ammonia or the basic acetate precipitation may be used. In either case the phosphoric acid accompanies the iron. The advantages in using the ammonia separation are the comparative ease of manipulation, and also, if the operation is conducted as just described, the filtrate is available for the determination of the sulphur. If, however, it is desired to use the filtrate for manganese or lime, the basic acetate separation must be used, and in that case the filtrate will be unsuited for the determination of the sulphur.

The mode of making the ammonia precipitation has been already described; to effect the basic acetate separation the procedure described in manganese mineral (Chapter XIII.) should be followed. As more iron is presumably present in the iron ore, it will be advisable to use 1 to 1.5 gms. of sodium acetate instead of 0.5 gms., as there recommended.

Determination of Phosphorus.—The line followed consists in dissolving the precipitate containing iron and phos-

phoric acid in nitric acid, separating the phosphoric acid from that, as ammonium phospho-molybdate, dissolving that precipitate in ammonia, and precipitating the last solution by addition of "magnesia mixture."

Dissolve the precipitate obtained either by ammonia or basic acetate in the manner already described, by transferring the most of it with the aid of a spatula to the vessel in which the precipitation was made, and afterward pouring hot dilute nitric acid through the filter onto the main bulk of the precipitate. Use what is equivalent to 25 or 30 c. c. of concentrated nitric acid, and then boil down in a No. 2 beaker to a bulk of 10 to 15 c. c. to expel all other acids. Dilute then with warm water to about 100 c. c. Then place in a No. 2 beaker about 40 c. c. of the molybdate reagent, and 15 to 20 gms. of crystals of ammonium nitrate, and filter the iron solution into it, stirring at the same time. The material retained by the filter should be trifling in amount, and should show no tinge of iron. If it does, some phosphoric acid is sure to be retained as well. Place the beaker on the boiling-water bath, and stir it every five or ten minutes, until the yellow precipitate of phospho-molybdate subsides with tolerable rapidity (in one or two minutes) after stirring. This will require about an hour. If too much free acid is present, the precipitate forms slowly and incompletely. Remedy this by adding ammonia, a few drops at a time and stirring vigorously, until the flakes of ferric hydrate redissolve very slowly in the hot solution. If too little free acid is present, the precipitate is likely to have a strong orange color, and it contains iron which cannot be washed out. In that case it will be more expeditious to carry the work along and to separate the iron by a reprecipitation, as will be described. Boiling the solution, or allowing it to stand for a long time is likely to cause a separation of pale yellow molybdic acid, which it is best to avoid. If the precipitate forms crusts on the side or bottom of the beaker, it will also contain iron, which must be separated.

Wash *by decantation* with a 10 per cent solution of ammonium nitrate, containing about one per cent of nitric acid, until 10 or 15 c. c. of the washings fail to show any dark coloration with ammonium sulphide. Be especially particular to wash the filter from the uppermost edge down. If the washing solution is too hot, a basic ferric nitrate may form in contact with the filter-paper, which is best removed by washing at a lower temperature. When the washing is apparently complete, neutralize the filtrate and washings partly with ammonia, and stand the beaker on the water-bath to recover any more precipitate which may possibly form. If after some time only a small precipitate of (nearly white) molybdic acid forms, the precipitation may be regarded as complete. If the precipitate is yellow, it must be filtered off and treated with the first precipitate. Place the beaker in which the precipitation was effected under the funnel used for filtration: then pour upon the filter 5 or 10 c. c. of diluted ammonia (1 to 3). Stronger ammonia is liable to form a protecting film of ammonium molybdate over the precipitate, and thus prevent its ready solution. On shaking the beaker containing the main bulk of the precipitate the latter should all go into solution, unless it is very large in amount, in which case a little more of the ammonia is poured through the filter. Both the filter and the ammoniacal solution should be absolutely free from the faintest yellow tinge of iron. If the iron has not been all removed, the addition of ammonia induces a recombination of ferric phosphate, which is of course not permissible at this stage. If iron is seen to be present, wash the filter with ammonia until it is judged that all of the molybdic acid has been removed. Then dissolve the iron through the filter into the same beaker by means of warm (not hot) dilute nitric acid, using eventually enough acid to overneutralize the ammonia, and to reproduce the conditions of the original precipitation. Heat on the water-bath, and stir as before. This second precipitation usually does not take so long as the first one.

Filter and wash as before, and finally dissolve the precipitate in ammonia. If some iron still shows, the operation must be repeated; but with moderate care, such repetition should be unnecessary. Now add to the ammonia solution of the precipitate enough concentrated hydrochloric acid to render it decidedly acid, and then enough ammonia to render it alkaline. This is for the purpose of obtaining ammonium chloride in the solution. Then *cool the solution* completely. On cooling, a slight flocculent turbidity may appear, owing probably to the presence of silica or similar impurity from the reagents, or perhaps to some separation of molybdic acid. If there is reason to suspect that much silica is present, the solution should be allowed to stand some time for it to separate. If not, filter as soon as cool through the original filter into a small beaker (No. 1 or smaller), wash two or three times with diluted ammonia, using as little liquid as possible. The aim is to obtain *all* of the phosphoric acid in as small a bulk of solution as possible (20 c. c. or less), in a solution perfectly *clear and bright*. Then add drop by drop, with stirring, 1 c. c. or more of magnesia mixture (chloride solution). The amount to be added will depend upon the proportion of phosphoric acid present, as judged from the bulk of the molybdate precipitate (1 c. c. of magnesia mixture will precipitate about 0.01 gm. P. The molybdate precipitate contains but little over 1.5 per cent of P). After stirring, allow to stand cold for some time, filter, and wash after the manner prescribed under magnesium sulphate for the manipulation of the magnesium precipitate (Chapter II.). If the precipitate begins to form promptly on the addition of the magnesium chloride it will separate completely in the course of an hour or more, otherwise it may not be safe to filter until the beaker has stood in ice-water for two hours or over. From the weight of the ignited precipitate calculate phosphorus. The element exists in iron ores as phosphate, but for the purposes of the iron master it is desirable to know the percentage of the element, since by

the usual metallurgical process all of the phosphorus in the ore will appear in the metal. "Phosphorus in Iron" is a phrase introduced into some reports, signifying the percentage of phosphorus which may be expected to be present in the iron obtained from the ore under examination. The figure is obtained by taking the percentage of iron as 100, and then calculating the ratio of phosphorus to it. Thus, suppose an ore showing 55 per cent of iron and 0.1 per cent phosphorus; then $55 : 0.1 = 100 : x$. $x = 0.182$ phosphorus in iron.

SEPARATE DETERMINATIONS.

Many analysts prefer to take separate portions of the ore for the determinations of iron, of sulphur, and of phosphorus, instead of making the analysis continuous, as in the plan just detailed. This mode of working has its advantages, such as avoiding the necessity of delaying one series of operations before another can be commenced, etc. Such methods may be here given.

Separate Determination of Iron.—Briefly this would consist in dissolving by the use of concentrated hydrochloric acid, reducing and titrating (to meet some cases), or decomposing by fusion with potassium bisulphate, dissolving, reducing, and titrating.

Most iron ores, if finely pulverized, will yield their iron to boiling concentrated hydrochloric acid. Some may contain minerals, such as hornblende, which are not decomposed by this treatment. In such cases the amount of iron left in the insoluble mineral is neglected as unimportant, or the insoluble portion is filtered off and fused with alkaline carbonates until it will yield to the acid, according to requirements.

Weigh out 1 gm. of ore (very finely pulverized), place it in a small casserole, add about 10 c. c. of concentrated hydrochloric acid, and boil for some minutes, until the indications are that all the iron has been completely

extracted. Do not allow the solution to get so far boiled away that it will spatter, but add more hydrochloric acid from time to time in sufficient quantity to avoid such a contingency. If the ore has been well pulverized, about 15 minutes boiling will amply suffice. If now the dichromate titration is to be used, all that remains to be done is to dilute to 100 or 150 c. c. with boiling water, reduce with stannous chloride, etc., and titrate with the standardized dichromate solution. (See Ammonia Iron Alum, Chapter IX.) The separation of the silica, etc., by filtration is unnecessary, unless it is required to extract the small amount of iron remaining in the associated mineral which has refused to decompose by this treatment, and still shows dark grains. In such a case, filter after dilution, incinerate the filter containing the insoluble residue in a platinum crucible, add 1 or 2 gms. of mixed sodium and potassium carbonates, fuse at a good heat for a quarter to half an hour, dissolve the melt in dilute hydrochloric acid, add the solution (without filtering) to the main solution, and reduce and titrate the whole. If the permanganate titration is to be used, expel almost all of the excess of hydrochloric acid by heating on the water-bath before diluting it, and then dilute with about 100 c. c. of sulphuric acid (1 of acid to 5 of water), reduce with zinc, add 20 c. c. of a 20 per cent solution of manganese sulphate, and titrate in a solution diluted to between 500 and 700 c. c.

If potassium bisulphate is used for decomposition, fuse 1 gm. of the ore with 10 or 12 gms. of the bisulphate as described in the first part of this chapter. The solution may be used directly for reduction with zinc and titration with permanganate, or (after addition of hydrochloric acid) for reduction with stannous chloride, etc., and titration with dichromate.

Separate Determination of Sulphur.—Fuse 1 (or more) gms. of the pulverized ore with five times its weight of mixed carbonates and 0.5 to 1 gm. of alkaline nitrate. After cooling the melt, boil with water and filter off the

oxides of iron, etc. Acidify the filtrate with hydrochloric acid, and evaporate to dryness to separate silica. Take up with about 20 c. c. of dilute HCl., filter and wash, bringing the bulk up to about 300 c. c. Boil this solution and, while boiling, add 5 to 8 c. c. of barium chloride solution, which has also been boiled for a few minutes. Stir well, and allow to stand for some hours. Filter, wash, ignite, and weigh as directed (Chapters I and II).

Some analysts prefer to dispense with the fusion. To work in this manner treat 1 to 5 gms. of the ore in a casserole with 10 c. c. of strong nitric acid, followed by 40 c. c. of concentrated hydrochloric acid. The nitric acid is indispensable to oxidize the sulphides, but must all be removed before the precipitation can be effected. Evaporate to complete dryness, moisten with 3 c. c. to 10 c. c. of concentrated hydrochloric acid, heat for 10 minutes on the water-bath, then dilute to about 300 c. c. with warm water, add the necessary quantity of fresh-boiled barium chloride solution, and allow to stand cold for several hours. In the presence of the iron the precipitation must be effected in a solution which is only warm (not hotter than can be borne by the hand), or it will contain iron, and it must be allowed to cool thoroughly, the barium sulphate being soluble in a hot solution of ferric chloride. After filtering the cold solution, wash the beaker and filter once with hot dilute hydrochloric acid, and then with cold water until all chlorides have been removed. Dry, ignite, etc., as before.

Separate Determination of Phosphorus.—Two methods will here be described, which with some modifications are also applied to manufactured irons as well: the "citric acid method," which however is regarded with disfavor by many, and Emmerton's volumetric method (*Trans. Am. Min. Eng.*, XV., 93).

The principles in the citric acid method are that ferric iron when precipitated carries phosphoric acid with it, that ferrous iron is not precipitated by the basic acetate method, and that the presence of citric acid in a solution

prevents the separation of ferric salts when that solution is made alkaline, but does not prevent the separation of magnesium ammonium phosphate.

For the citric acid method, treat 5 or 10 gms. of the ore with concentrated hydrochloric acid. As the phosphorus is present in iron ores in the form of phosphate (usually in combination with lime or with iron) it may be taken into solution by this means, except in the case of certain ores. Evaporate to dryness, remove silica, etc., and take up with hydrochloric acid.

Dilute the solution with cold water to about 500 c. c. and partially neutralize with ammonia or with sodium carbonate, add about 5 c. c. of ammonium bisulphite solution, stir it in well, and heat gradually to boiling. The color of the solution should eventually change to the pale green of the ferrous salt, but it should be clear, with the exception of the insoluble silica, etc., from the ore.

Boil out the sulphurous acid, hastening its expulsion if need be by passing a current of carbon dioxide through the solution. By this time *some* of the iron may have reoxidized to the ferric form. It may, however, be advisable to add 10 or 15 c. c. of the standard solution of potassium permanganate to insure the presence of some ferric iron.

Then add 5 c. c. of a saturated solution of sodium acetate and boil. A precipitate consisting of ferric phosphate with some hydrate should then form. It should be red, indicating the presence of an excess of ferric hydrate. If it has the light buff-colored tint of ferric phosphate, all of the phosphoric acid may not be present in the precipitate. Filter quickly. The filtrate should be clear and bright in the stem of the funnel, but in contact with the air the iron rapidly oxidizes to a sufficient extent to render it turbid. If for any reason it is suspected that all of the phosphoric acid may not have been carried down in the first precipitate, add to the filtrate about 10 c. c. more of the permanganate, and boil and filter again.

Dissolve the precipitated ferric hydrate and phosphate

in hydrochloric acid, evaporate off the excess of acid, and then add a clear solution of 5 or 10 gms. of citric acid.

Now on rendering the solution alkaline with ammonia no precipitate should appear. If it does, more citric acid is required.

Finally, add a few c. c. of "magnesia mixture," and allow it to stand to precipitate. Further details are unnecessary, except that in this case it is advantageous to add some ammonium nitrate to the ammoniacal washing solution.

The essential feature of Emmerton's volumetric method consists in precipitating the phosphorus as ammonium phospho-molybdate under carefully regulated conditions, so that the precipitate shall contain phosphorus and molybdic acid in definite proportion 1 : 12, *i. e.*, $12\text{MoO}_3(\text{NH}_4)_2\text{PO}_4 + x\text{H}_2\text{O}$, dissolving the precipitate, and reducing the molybdic acid by means of zinc, and then titrating with potassium permanganate, which restores the MoO_3 to its original form.

The steps are: 1. **Dissolve** a weighed amount of the ore **in concentrated hydrochloric acid**. With ores containing much phosphorus, nearly or quite 1 per cent, 1 gm. will suffice. With purer ores, more may be taken. The maximum amount necessary may be put at 10 gms. **Evaporate to small bulk** (10 or 15 c. c.).

2. **Add 40 c. c. of strong nitric acid and evaporate down to about 15 c. c.** The object is to obtain a nitric acid solution in which to effect the precipitation. If the nitric acid solution is allowed to go to dryness it affords ferric oxide insoluble in nitric acid, which always retains some phosphate. This can only be brought into solution by hydrochloric acid, which must be removed by addition of more nitric acid, and evaporating.

3. **Dilute and filter into an Erlenmeyer flask** of about 400 c. c. capacity, **bringing the solution up to about 100 c. c.** Time may often be saved by transferring the solution, insoluble portion and all, to a 100 c. c. flask, filling with water to the mark, and after *thorough mixing* allowing to

stand and settle, and then drawing off 80 c. c., which is filtered and used in the subsequent operations, the calculation in that case being of course based upon four fifths of the amount originally taken.

4. Add 20 c. c. of ammonia and then 5 c. c. of strong nitric acid (31 gr. 0.96). The object in this addition is twofold: To neutralize *a portion* of the free nitric acid, that the precipitation may not be retarded on that account, and to introduce some ammonium nitrate, which facilitates the precipitation. With practice, one can learn to judge by the color of the solution whether the conditions are right. **Dilute to about 250 c. c.**

5. Heat (or cool) to 85° C. Experiments have shown that the precipitation occurs most rapidly and satisfactorily at between 65 and 80° C. At lower temperatures it is too slow; at higher temperatures some molybdic acid may accompany the precipitate. By heating to 85° C., allowance is made for the cooling effect of the molybdate reagent which is added.

6. Add at once 40 c. c. of the molybdate reagent. Close the flask with a rubber stopper.

7. Wrap the flask in a towel, and shake for five minutes.

8. Filter through a rapidly running filter, and **wash with warm water containing 2 per cent of sulphuric acid and 10 per cent of ammonium sulphate.** If nitric acid and ammonium nitrate were used, as in the gravimetric process, the subsequent reduction with zinc might give some nitrous acid, which would use up some permanganate, and give erroneous results in the titration.

9. Dissolve through the filter with 30 c. c. of dilute ammonia (1 to 4) into a flask containing 20 gms. of zinc shot. If unamalgamated zinc be used, the platinum may be dispensed with. In that case, however, a blank test must be made with a corresponding amount of zinc to determine the amount of permanganate destroyed by the iron or other impurity in the zinc, and a correction must

be made. The reductor (see Chapter IX.) is frequently used in place of this and the two succeeding steps.

10. **Add 100 c. c. of dilute sulphuric acid (1 to 5), and heat on the sand-bath or iron plate for fifteen minutes.**

The color of the solution passes through pink, plum, pale olive-green to dark olive-green. As soon as it is poured from the flask it assumes a port-wine color, though this change of tint does not appear to indicate any appreciable oxidation of the molybdenum compound ($\text{Mo}_{12}\text{O}_{22}$).

11. **Filter through a plaited filter** containing a few fragments of zinc to keep up the reducing action. Wash two or three times with water. The final bulk of the solution will be about 400 or 500 c. c.

12. **Titrate with standard potassium permanganate solution.** The color of the solution, at first quite intense, becomes paler, and eventually colorless, when a slight excess of the permanganate gives its own peculiar pink tinge.

After deducting the permanganate destroyed by impurities in the zinc (*vid.* 9), should that be necessary, the phosphorus must be estimated. If the precipitate had the correct composition ($24\text{MoO}_3 : \text{P}_2\text{O}_5$ or $12\text{MoO}_3 : \text{P}$) 1 c. c. of a permanganate solution which = 0.006141 Fe represents 0.0001 P. If the permanganate solution has a different value in iron, the phosphorus value may be calculated by a simple proportion, *e. g.*: Suppose 1 c. c. = 0.0056 Fe; then

$$0.006141 : 0.0001 = 0.0056 : x. \quad x = 0.0000912 \text{ P.}$$

The permanganate should be standardized by trial on a sample in which the phosphorus has been determined gravimetrically. Arsenic and titanous acid in iron ores interfere with this method, the former by forming an arsenio-molybdate, and thus being reckoned as phosphorus, the latter by separating more or less completely from the solution when heated, carrying with it some phosphoric acid. The modifications which it is necessary to introduce in order to prevent such interference when one or the other of these elements are present, increase very materially the time required for the operation.

CHAPTER XV.

COMPLETE ANALYSIS OF IRON ORE.

The possible constituents in iron ores have been already enumerated. A complete determination of each and every constituent of an ore is seldom required. Moreover, all of the possible constituents are rarely, if ever, present simultaneously.

The information sought with regard to an ore is frequently most conveniently obtained by the examination of separate portions for certain constituents, and it is seldom necessary to follow out a comprehensive scheme of work. The following plan, however, may be suggested for ores containing titanium where several of the constituents are to be determined :

a. Fuse 5 (to 7) gms. ore with 25 gms. KNaCO_3 and 0.5 to 1.5 gm. alkaline nitrate.

b. Dissolve in HCl , evaporate to dryness, redissolve in HCl , and filter.

Residue <i>c.</i> Ignite, weigh. Expel SiO_2 by HFl and H_2SO_4 , fuse residue with NaKCO_3 , dis- solve in HCl and add to Solution <i>c.</i> (Ba SO_4 ?).	Solution <i>c.</i> Make up to known bulk, mix, and take out an amount corresponding to 1 gm. <i>d.</i> <i>d.</i> Reduce by SnCl_2 , and titrate Fe by $\text{K}_2\text{Cr}_2\text{O}_7$.	Remaining solution divide into portions representing <i>e.</i> 1 gm., <i>f.</i> 3 gms. (and <i>x</i> reserve). <i>e.</i> (Pass H_2S if necessary, filter, follow by reoxidation.) Make basic acetate separation. (Filterate may serve for Mn, etc.) Redissolve ppt. in HCl , precip. by ammonia, ignite, and weigh Fe_2O_3 , Al_2O_3 , P_2O_5 , TiO_2 (Cr_2O_3).	<i>f.</i> Make basic acetate separation. Precipitate <i>g.</i> Dry, and fuse with Na_2CO_3 for separation and determination of TiO_2 and P_2O_5 .	Solution <i>g.</i> For Mn, Zn, Ni, Co, Ca, and Mg.
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a. The suggestion as to the use of more than 5 gms. of ore to meet certain cases where the proportions of some

constituents are small, or to provide a reserve solution in case of accidents, as well as the use of the fluxes, have been explained in the preceding chapter.

b. If barium is present in the ore, it may prove convenient to add to the solution, while evaporating, a few drops of sulphuric acid, in order that the whole of that element may be left in the insoluble residue *c*. When titanium is present, some TiO_2 separates during the evaporation, giving a characteristic appearance to the solution. In separating the titanous acid carries with it ferric oxide, alumina, and phosphoric acid.

Residue c.—On account of the contamination of the silica when titanium is present, it is always necessary to determine it by loss, after expulsion with HFl , as described previously. The addition of an excess of sulphuric acid is in this case especially important, since otherwise TiF_4 would be formed and be volatilized with the silicon fluoride.

The non-volatile residue may usually be rendered soluble by fusion with alkaline carbonates and subsequent treatment with hydrochloric acid. In case barium sulphate is present, however, that compound will remain undissolved in the hydrochloric acid, and must be filtered off. If more than a mere trace is present, fuse it for a few minutes with alkaline carbonate, which will afford barium carbonate (soluble in hydrochloric acid) and alkaline sulphate (soluble in water). Leach out the sulphate with water, dissolve the barium carbonate in hydrochloric acid, and precipitate it with sulphuric acid for weighing.

Solution c.—It will be unnecessary to separate members of the hydrogen sulphide group in the portion taken for the titration of the iron. In the portion taken for other determinations they should be removed if present.

Solution d.—If barium is absent and no sulphuric acid has been added during evaporation, it will be possible to use this portion for the sulphur determination as well as for the iron, in the manner described in the preceding

chapter. It may, however, be found more convenient to take a separate portion for the determination of the sulphur as described (p. 115, viz., fusion with alkaline carbonate and nitrate, leaching out with water, and determining sulphur in the water solution). The dichromate titration is preferable in this case, since the stannous chloride does not reduce titanous acid and cause an interference with the correct estimation of the iron. When zinc is used, as in the ordinary reduction for titration with permanganate, titanous acid will reduce to Ti_2O_3 , which will take oxygen from the permanganate to form TiO_2 , and thus cause error. Sulphurous acid or hydrogen sulphide do not reduce the titanous acid, and may be used preliminary to the permanganate titration, provided the excess of either reagent is boiled out before titrating. When sulphurous acid is used, the flask in which the reduction is made must be fitted with a cork and tubes arranged in such a manner that a current of carbon dioxide may be passed through the boiling solution to expel the excess of sulphurous acid without allowing any iron to reoxidize. Hydrogen sulphide is more conveniently managed. A rapid current of the gas is passed through the solution, which has been placed in a flask with a narrow neck. After the solution has been saturated with the gas and complete reduction of the iron has taken place, bring the solution to a boil quickly, and keep up a brisk ebullition until the separated sulphur granulates, and the escaping steam causes no stain on paper moistened with lead acetate. Dilute with cold water and titrate immediately.

The precautions as to presence of an excess of sulphuric acid, cold titration, and dilute solutions, etc., in case of the presence of hydrochloric acid must be carefully observed in the titration with permanganate.

The division of the remaining portion of the solution had best be arranged according to requirements. It is well to have a portion in reserve in case of accidents, to obviate the necessity for the repetition of the previous steps, or for

the sake of duplication of certain determinations. The portion for determination of the combined weights of Fe_2O_3 , Al_2O_3 , P_2O_5 , and TiO_2 (*Solution e*) should represent not less than 0.5 gm. or more than 1 gm. of the ore. For the determination of titanitic acid what represents 1 gm. is in many cases sufficient, but for determining phosphorus what represents at least 3 gms. is desirable, unless the percentage of phosphorus is unusually high. As the compounds of the two elements are separated with difficulty, it is preferable to take a proportion in which it may be possible to determine the phosphorus.

Solution e.—If the solution contain copper, arsenic, or other members of that group, they must be separated by hydrogen sulphide and filtered off. The precipitate may be used for the determination of those elements if they are present in sufficient quantity. Hydrogen sulphide also reduces the iron to the ferrous form with separation of sulphur, and as the succeeding operation requires that the iron shall be in the ferric condition, a reoxidation is necessary. Potassium chlorate is preferred by some for this purpose, nitric acid by others. Boiling is necessary in either case. The use of the last-named reagent has the advantage that, so long as any ferrous iron remains in the solution, a blackish coloration is temporarily developed on adding a few drops of the acid, whereas with the chlorate one can only surmise when the oxidation is complete. The solution should be boiled until the separated sulphur granulates so that it may be filtered out. Time is saved by boiling the solution *previous* to adding the oxidizing agent until there is little or no odor of hydrogen sulphide. The boiling tends to precipitate some of the titanitic acid, although the influence of the hydrochloric acid is to keep it in solution. The precipitate of sulphur should be ignited, and if any titanitic acid remains, that should be brought into solution by the aid of fusion and added again to the solution.

The basic acetate separation is conducted essentially as

described in Chapter XIII. As more iron is presumably present than in manganese minerals, a larger amount of sodium acetate must be used (1 to 1.5 gms.). The precipitate cannot readily be washed free from alkaline salts, so that it is necessary to redissolve and reprecipitate with ammonia. Chromium oxide will appear in the basic acetate precipitate, since the iron is presumably present in large proportion. The existence of chromium and titanium in the same ore is, however, unusual. The object in weighing the precipitate obtained is to determine the alumina by difference, the other constituents of the precipitate being determined in other places.

As some of the alumina may have escaped precipitation as basic acetate, it is well to evaporate the filtrate to dryness, and then to take up with acetic acid, to recover in the insoluble form the last portions of the alumina. This residue of alumina may be dissolved in hydrochloric acid and the solution added to the main one.

Direct determination of the alumina is, however, sometimes resorted to. At least three different methods may be here described: 1. Caustic alkali; 2. Tartaric acid; and 3. Hyposulphite method.

1. In the first the mixed oxides (such as would result from the ignition of the basic acetate precipitate) are fused in a silver crucible with caustic alkali (soda or potash) to convert the alumina into alkaline aluminate, which is leached out with water, and from the filtered solution the alumina is precipitated by neutralizing with hydrochloric acid and addition of ammonia. Titanic acid, if present, remains with the ferric oxide. The method has the disadvantage of requiring a silver crucible and caustic alkali absolutely free from alumina, which it is difficult to obtain in all cases. The method of precipitating the solution of the oxides with excess of caustic alkali, without resort to fusion, is still more liable to error.

2. The tartaric acid method depends on the fact that tartaric acid prevents the precipitation of alumina and iron

as hydrates on addition of alkali, but does not prevent the separation of the iron as a sulphide by alkaline sulphide; whereas alumina, not forming a sulphide in aqueous solution, is not precipitated under these conditions.

Add to the hydrochloric acid solution of the oxides at least 2 gms. of tartaric acid for every gram of iron ore represented, and render alkaline with ammonia. If any turbidity appears, the amount of tartaric acid is insufficient, and should be increased. Then to the clear solution add ammonium sulphide, or pass hydrogen sulphide until the iron is all precipitated as sulphide. If the amount of alkaline chloride is sufficient, the iron sulphide separates readily from the *yellow* solution. If it is not, the solution has a greenish cast, and the iron sulphide deposits slowly. Add ammonium chloride if necessary, filter, evaporate the clear solution to dryness, add sodium carbonate, and ignite to destroy the tartaric acid. The final destruction of the organic acid may be facilitated by the addition of a little alkaline nitrate, and fusing. Take up with acid, and precipitate the alumina by ammonia as usual. If titanium is not present, dilute hydrochloric acid may be used for effecting solution. If titanium is present the melt must be dissolved in sulphuric acid, sodium acetate and acetic acid added, and the solution boiled for 15 to 20 minutes to separate titanous acid, which may be ignited and weighed if desired. In the filtrate the alumina may be precipitated by ammonia, the separation of which will be facilitated by the addition of a little ammonium sulphide.

In the hyposulphite method the alumina is separated as phosphate from a solution containing sodium acetate, in which the iron has been reduced by hyposulphite. It is inapplicable in presence of titanous acid, since that also precipitates as phosphate, which on washing parts with an indeterminable amount of phosphoric acid. To the solution of the oxides nearly neutralized (cold) with sodium carbonate is added 5 to 10 c. c. of a saturated solution of sodium hyposulphite, and heat is applied. The color

passes through violet to colorless, thereby indicating that the iron has been reduced. Then about 5 c. c. of a strong solution of sodium acetate, and 3 to 4 c. c. of hydrodisodic phosphate solution is added, and the solution is boiled for about an hour, until there is no odor of sulphurous acid. Alumina phosphate, containing possibly a little ferric phosphate, separates, together with sulphur. This precipitate is filtered off, dissolved (with exception of the sulphur) in hydrochloric acid, the solution nearly neutralized, and treated as before with hyposulphite, followed by acetate and phosphate. The precipitate from this second treatment is usually pure alumina phosphate $[Al_2(PO_4)_3]$, and may be filtered off, washed with hot water, dried, ignited, and weighed. Excessive washing is to be avoided. Calculate to Al_2O_3 .

Solution f (representing at least 3 gms.).—This solution may be treated with hydrogen sulphide if necessary, as in the case of solution *e*.

It is of advantage to make the division first, and to treat the two divisions separately, since the solution resulting from reoxidation will be too warm to be divided with accuracy.

Solution g.—After making the basic acetate separation, the solution is in suitable condition for the determination of manganese, lime, magnesia, zinc, nickel, cobalt, if the last three are present. The first three are rarely absent.

If only manganese and the alkaline earths are present, the manganese may be separated by bromine as in manganese mineral, and in the filtrate the lime and magnesia may be determined as in limestone analysis. If zinc, nickel, etc., are present, it may be found convenient to separate the members of the ammonium sulphide group by use of that reagent, and to dissolve the separated sulphides for further separation and determination, by methods described under the analyses of their respective ores.

Precipitate g is to be fused with sodium carbonate (not

potassium carbonate) in order to obtain soluble phosphate and insoluble titanate, the iron remaining with the latter. A liberal amount of the flux and a tolerably long fusion is necessary to effect the change completely. The precipitate is dried and pulverized, and, as may be convenient, the whole or some aliquot portion is taken, and mixed in a platinum crucible with three to five times its weight of dry sodium carbonate and the mass heated to fusion for at least two hours. After cooling the melt is boiled with water, filtered, and washed until the washings begin to run turbid, which occurs as soon as the most of the alkaline carbonate has been removed. The insoluble material is again dried and fused as before. The solution from the second fusion should show no yellow precipitate of phosphomolybdate on acidifying with nitric acid and addition of molybdate mixture. If it does, a third fusion will be necessary.

This is usually unnecessary, but the treatment needs to be repeated until no more phosphoric acid can be extracted. The solutions will contain chromium as alkaline chromate, if that element exists in the ore. All the solutions from this treatment which contain phosphate must be acidified with nitric acid, and the separation by molybdate solution and final precipitation by magnesium carried out in the manner already given (p. 111). If arsenic is present, and has not been previously separated, the magnesium precipitate should be dissolved in hydrochloric acid, and the solution treated with hydrogen sulphide to precipitate that element, before rendering it again ammoniacal for the purpose of precipitating the ammonium magnesium phosphate.

The material from the fusion which is insoluble in water is dissolved in sulphuric acid with liberal addition of sulphurous acid, or a sulphite to reduce the iron. Then, after nearly neutralizing with sodium carbonate, and addition of about 5 gms. of sodium acetate, besides about 40 c. c. of strong acetic acid, the solution is boiled for 15 to 20

minutes, until the precipitate of titanous acid granulates sufficiently to separate readily. This first precipitate is usually contaminated with some ferric oxide. Redissolve in a very little concentrated hydrochloric acid or in sulphuric acid; add successively sulphurous acid, sodium carbonate—acetate, and acetic acid as before, and boil again. It is then usually sufficiently pure to be filtered, washed, ignited, and weighed as TiO_2 .

SEPARATE DETERMINATIONS.

Water, as hygroscopic moisture, may be determined by drying some of the ore to constant weight in an air-bath at 110° . That present in combination should be determined by direct weight, after the method described under hydrodisodic phosphate (Chapter VIII.). In many cases a direct ignition of the ore will cause changes in weight not entirely due to loss of water (loss of carbon dioxide, oxidation of ferrous iron, etc.), so that a direct determination is usually necessary.

Carbon dioxide may be determined by methods described in the analysis of calcium carbonate (Chapter III.).

Chromium is usually best determined in a separate portion, the method being given under analysis of chromite (Chapter XVI.).

Arsenic may be determined by fusion with alkaline carbonate and nitrate as directed for the separate determination of sulphur, leaching out the sodium arsenate and other soluble salts with water, and in the solution precipitating by hydrogen sulphide after acidification with hydrochloric acid. (See Arsenic ore.)

Copper.—Bring 10 gms. of the ore into solution by the aid of fusion, as already described. Partially neutralize the acid solution, add sodium hyposulphite in excess, and boil. Cuprous sulphide mixed with sulphur, etc., will separate. Ignite the precipitate to remove sulphur, arsenic, etc., dissolve the residue in sulphuric acid with a

few drops of nitric, and electrolyze. (See Copper ore, Chapter XXII.)

Appendix 3.—Vanadium and tungsten have been found in iron ores.

To determine vanadium, fuse 15 or 20 gms. of the ore, in the form of impalpable powder, with one third its weight of potassium nitrate. Then cool, and remove the mass from the crucible by digesting with water as usual, and mix carefully with nitric acid, leaving the solution slightly alkaline. Filter, and add to the filtrate barium chloride as long as it produces a precipitate. Filter out the baryta salts; to the still moist precipitate add dilute sulphuric acid in slight excess, boil and filter. Then neutralize the filtrate with ammonia, concentrate, and add a fragment of ammonium chloride. As the ammonium chloride dissolves, ammonium vanadate is precipitated, as a crystalline powder. Allow it to settle, filter it out, and wash it with solution of ammonium chloride. Dry the precipitate, and heat it to red vanadic acid, which fuses, and cools to a crystalline mass. (H. Rose, *Quant. Anal.*, pp. 498, *et seq.*)

To determine tungsten, fuse 15 or 20 gms. of the finely pulverized ore with four times its weight of sodium carbonate. (Do not use nitrate.) Digest the fused mass with water, filter, and wash. Saturate the solution carefully with nitric acid, so that it will slightly redden litmus paper, after the carbonic acid has been expelled. Let it stand 24 hours in a moderately warm place, and then, but not before, add solution of mercurous nitrate, then a little HgO mixed with water. Let the precipitate settle, collect it on a filter, and wash with water, to which has been added a little mercurous nitrate. This is necessary to prevent the liquor from running through the filter turbid. After drying, burn the precipitate under a chimney with a good draught. After calcination, tungstic acid remains pure. Repeat the ignition to constant weight. (See H. Rose, *Quant. Anal.*, p. 488.)

Ferrous iron oxide as distinguished from ferric oxide may be sometimes required in the analysis of iron ores and minerals. The principle involved in the methods for its determination involve simply effecting solution by means of a non-oxidizing acid, and exclusion of the oxidizing influence of the air. When solution under these conditions has been effected the titration may be conducted in the ordinary manner.

Pulverize the ore finely, introduce an accurately weighed quantity (1 gm. or more) into a flask, arranged so that a current of carbon dioxide gas or illuminating gas may be passed through it, add 10 or 20 c. c. of concentrated hydrochloric acid, and apply heat until the ore has been decomposed, so far as possible. Disconnect the flask, filter rapidly through asbestos, and dilute and titrate the solution directly (preferably with dichromate). If it is desired to determine the ferrous iron in the portion insoluble in hydrochloric acid, transfer asbestos and all to a platinum crucible, add some 10 c. c. of hydrochloric acid and about 5 c. c. hydrofluoric acid, place the crucible on a water-bath, and invert over it a metallic funnel (lead or other). Connect the carbon dioxide generator with the funnel in such a way that the crucible will be surrounded by a non-oxidizing atmosphere. Heat until both asbestos and residual ore are dissolved and hydrofluoric acid has been expelled, then rinse into a beaker, and titrate as before. (*Vid. Chem. Analysis of Iron*, etc., Blair, 2d Ed., p. 217.)

The method of separating phosphoric acid and titanatic acid mentioned in description of manipulation of *g* may be applied directly to the (titaniferous) ore itself in case only these constituents are to be determined. 2 gms. (or more) of the finely pulverized ore may be fused with 10 gms. of **sodium carbonate** to separate the phosphoric acid as **sodium phosphate** (soluble in water) from the **sodium titanate** (insoluble). With the ore the fusion needs to be longer than in the case of the basic acetate precipitate to

effect complete separation. A second fusion is of course necessary, as before, to prove that the first was completely effective. It may be advantageous to add some sodium nitrate in the first fusion to effect complete oxidation of the iron, some of which is usually in the ferrous form in titaniferous ores.

The water solutions from the fusion will contain more or less of the silica in the ore, and must be evaporated to dryness after acidification with nitric acid, and redissolved in nitric acid and water, before proceeding to the separation and determination of the phosphorus.

CHAPTER XVI.

ANALYSIS OF CHROMITE.

Chromite, the mineral source of the chromium compounds used in the arts, has the composition $\text{FeO} \cdot \text{Cr}_2\text{O}_3$. The theoretical composition is :

FeO , 32

Cr_2O_3 , 68

Magnesia, silica, and manganese are frequently present, but the full list of possible constituents of the mineral is essentially that given for iron ores. With this mineral, however, the chromium is usually the important constituent, and the determination of chromic oxide only is made. The plan of procedure is, in brief :

- a.* Fuse 0.5 to 1 gm. with Dittmar flux.
- b.* Dissolve in water, filter, add 3 to 5 gms. NH_4NO_3 , and evaporate to dryness, acidifying with HNO_3 toward the end of the operation.
- c.* Dissolve, filter, add HCl and SO_2 , boiling out SO_2 .
- d.* Neutralize with ammonia and boil, adding a few drops of $(\text{NH}_4)_2\text{S}$. Redissolve in HCl , and reprecipitate with ammonia as before, to purify the precipitate. Ignite and weigh Cr_2O_3 .
- a.* Chromite is very refractory, and requires to be pulverized very finely in order that decomposition may be readily effected. Elutriation of the partially pulverized sample is not to be recommended, since the specific gravity of the mineral is so high that a material which does not fairly represent an average of the sample is likely to result.

The Dittmar flux is obtained by fusing together two parts of borax glass and three parts of dry sodium and potassium carbonates mixed approximately in the propor-

tions of their molecular weights (106 to 138). After fusing, the mixture is poured upon a cold surface, and when cool, broken up for use. As it is somewhat hygroscopic, it should be kept in a tightly corked bottle. When fused, this flux is somewhat pasty, holding the mineral partly in suspension, and thus favoring its decomposition. An active agent in the decomposition of chromite is the oxygen of the air, which converts the chromium to chromate in presence of the alkali of the flux—a fact utilized in the manufacture of chromium compounds from the mineral. From the facts presented, the reasons for the following procedure will be apparent.

Fuse in a shallow platinum dish five or six times as much Dittmar flux as it is intended to take of ore, and allow it to cool. Then weigh out in a watch-glass 0.5 to 1 gm. of the chromite, and by means of a feather brush it onto the surface of the melt, spreading it as evenly as possible. Fuse in the flame of a good Bunsen burner, stirring the melt occasionally with a platinum wire, until decomposition has apparently been effected. This is likely to require about forty minutes if the ore has been well pulverized and the stirring has been sufficiently frequent. If either of these points has been neglected, it may require a much longer time. Remove the heat temporarily, and as the mass cools stir with the platinum wire in such a way as to take a portion of the material from the bottom of the melt. As soon as it hardens sufficiently, withdraw it and examine it as it cools for black grains of undecomposed ore. If any are seen, replace the test bead in the dish, cover the same, and apply heat. The material soon melts off from the wire, when the cover may be removed, unless the heat is insufficient to keep the mass fluid without its use. When the decomposition seems to be complete, allow the melt to cool.

b. The material soluble in water, besides the excess of the constituents of the flux, may be alkaline chromate, manganate, aluminate, and silicate. It is desired to re-

move all of the latter except the chromate. Evaporation with ammonium nitrate will cause the manganese to assume the form of insoluble MnO , and at the same time precipitates the alumina, which, with the prolonged heat, assumes a form practically insoluble in nitric acid, especially when hot. The addition of nitric acid, and evaporation to complete dryness, renders the silica also insoluble, so that by the subsequent filtration all of those substances may be removed.

c. In the solution from the evaporation the addition of sulphurous acid and boiling readily reduces the chromium to the form of base, especially when some strong acid, as hydrochloric, is present. Hydrochloric acid also serves another end by affording alkaline chloride, which favors the separation of the precipitate of $Cr_2(OH)_6$.

d. On neutralization of the hot solution with ammonia, it frequently happens that no precipitate will at first appear, but on boiling off the slight excess of ammonia which may have inevitably been added, the chromium hydrate separates. The separation may be facilitated by the addition of a little ammonium sulphide. The precipitate produced in presence of salts of the fixed alkalies is, however, never sufficiently pure to be at once ignited and weighed. After washing, it requires at least one re-solution in hydrochloric acid and reprecipitation to obtain it fairly free from contaminants. A third or even a fourth re-solution and reprecipitation may be advisable.

Calculate and report percentage of Cr_2O_3 .

If alkaline salts remain with the precipitate, they not only may add their own weight to that of the precipitate, but, with the access of air, may induce a further increase of weight due to the partial formation of alkaline chromate.

Recently sodium peroxide has been introduced as a laboratory reagent, and is of especial service in decomposing chromite.

Weigh 0.5 gramme of the *finely pulverized* ore in a small nickel crucible, add about 2 grammes of the dry peroxide, and mix thoroughly with a platinum wire. By means of a feather brush any adhering particles back into the crucible. Very siliceous ores will require a larger proportion of flux. Support the crucible (uncovered) on a nickel triangle, and apply a low flame of a Bunsen burner. Only the (colorless) tip of the flame should touch the bottom of the crucible. In about two minutes the mass should be in quiet fusion. Allow it to remain so for eight or ten minutes, then hold the crucible by the tongs in a stronger flame, to bring it up to full red heat, at the same time moving it so as to give the contents a rapid rotary motion. Keep this up for a full minute. When cold, lay the crucible on its side in a small casserole, and throw into it a stream of boiling hot water from a wash bottle. 50 c. c. will usually suffice.

A vigorous effervescence of oxygen ensues. Turn the crucible about with a rod until all chromate has been dissolved, rinse it off, and boil the solution for about five minutes to completely decompose all peroxide. Filter into a half-litre flask, washing the black Ni_2O_3 , etc., with cold water until the washings run colorless. When the solution is cold, dilute to the mark, mix well, and use 250 c. c. at a time for determination of chromium.

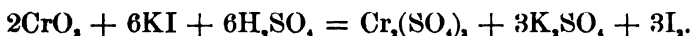
The black insoluble residue (paper and all) should be digested warm for some time in about 20 c. c. of diluted sulphuric acid. No black grains of undecomposed ore should remain. If a determination of silica is required, the black coating on the inside of the crucible should also be dissolved off in the same way, and the united solutions evaporated. The water solution of the chromate should also be acidified and evaporated.

Volumetric.—The methods are based upon the measurement of the oxidizing power of the chromate, after all of the chromium in a known amount of ore has been converted to that form. The preliminary treatment may introduce

other oxidizing agencies (ferric iron, manganate, permanganate, hypobromite, etc.), which must be eliminated. Ferric iron can be filtered off from the alkaline solution. Manganate or permanganate may be destroyed by boiling the alkaline solution after addition of hydrogen or sodium peroxide, or else by evaporating with ammonium nitrate. In any case, filter off the resulting manganese oxides. Remove hypobromite, etc., by acidifying and boiling.

To titrate the chromium many English analysts add a known amount (excess) of a ferrous salt (Ferrous ammonium sulphate) to the acid solution, and then titrate back the excess by standard permanganate or dichromate.

Titration by standard sodium hyposulphite through the medium of potassium (or sodium) iodide is preferable. A convenient strength is 30 grammes of crystallized hyposulphite per litre (1 c. c. = about 0.003 gm. Cr_2O_3). Standardize by weighing out 2 grammes of potassium dichromate (= 1.035 grammes Cr_2O_3), dissolving in 100 c. c. of water, and titrating lots of 10 c. c. at a time (cold). Dilute each lot to about 200 c. c., add about 10 c. c. of dilute sulphuric acid, and then 10 c. c. of a ten per cent solution of potassium iodide. The chromium is converted to sulphate, a corresponding amount of iodine being set free, thus:



This is titrated by the sodium hyposulphite in the same manner and with the same precautions as described (copper ore, Chapter XXII., p. 207). High dilution is necessary to render the final destruction of the starch iodide easily perceptible.

To titrate the solution of chromate from an ore, add first an excess of dilute sulphuric acid. In a solution from a sodium peroxide fusion (obtained as above), representing about 0.25 grm. of the ore, 15 to 20 c. c. will suffice. Then add about 15 c. c. of the iodide solution, dilute to 800 or 900 c. c., and titrate cold in the manner described.

CHAPTER XVII.

ANALYSIS OF SLAGS.

The analysis of slag is of great importance to the metallurgist as a guide in making up his charges, indications as to the working of the furnace, etc., and in many metallurgical works a daily examination of the slags is deemed necessary.

Two distinct and separate objects may be aimed at: 1. To determine whether the ratio of the bases and silica is suitable; in other words, whether proper proportions of the various ores and fluxes are being used. 2. To determine the presence and proportions of certain constituents with a view to deciding as to losses experienced, or as to the utilization of the slags for certain purposes.

The composition of slags in the iron industry (blast-furnace "cinder"), according to Phillips (*Elements of Metallurgy*, p. 192), ranges between $3(\text{CaO.SiO}_2).\text{Al}_2\text{O}_3.3\text{SiO}_2$ and $3(2\text{CaO.SiO}_2).2\text{Al}_2\text{O}_3.3\text{SiO}_2$, taking CaO as the type of the protoxide bases (sometimes put as RO) and Al_2O_3 as the type of the sesquioxide bases (R_2O_3). In these the ratio of oxygen in the bases to that in the silica ranges from (1:2) ("bisilicate") to (1:1) ("singulo-silicate"). It is often necessary to reckon more particularly; ratio of O in RO bases : O in R_2O_3 bases : O in SiO_2 . Bodemann's slag (loc. cit.), $4(\text{CaO.SiO}_2).\text{Al}_2\text{O}_3.3\text{SiO}_2$, is said to be still more fusible than those given above. In this the ratio of oxygen of bases to that in SiO_2 is the same as the formula first mentioned (1:2), but the ratios of RO and R_2O_3 are different.

"Percy's slag," which is sometimes used, has the formula $2(3\text{RO.SiO}_2).\text{R}_2\text{O}_3.\text{SiO}_2$ (*Notes on Assaying*, Ricketts,

Iron Assay). Calculating RO as CaO and R₂O, as Al₂O₃, the percentage composition of these slags would be :

	Phillips.	Bodemann.	Percy.
CaO.....	26.7 to 37.3	30	47
Al ₂ O ₃	16.2 " 22.7	14	15
SiO ₂	57.1 " 40.0	56	38

In the lead-silver industry the metallurgists usually calculate for percentages of constituents. As a general statement the range of composition is put as follows :

SiO ₂	30 to 34 per cent.
Fe and Mn.....	25 to 30 " "
CaO, MgO, and BaO	18 to 24 " "
Zn.....	1 to 6 " "

Slags of certain types are aimed at according to circumstances (*vid.* "Lead Slags," by M. W. Iles, *Chemical News*, LVII, 1888, p. 4; also cf. "Calculation of Lead Blast-furnace Charges," H. V. Furman, *S. of M. Quarterly*, XIV., 134). The types given by Iles are :

Type.	A	B	C	D	E	F	G
CaO, (MgO, BaO)....	6	10	12	16	20	24	28
FeO and MnO.....	52	45	50	34	40	33	27
SiO ₂	32	35	28	34	30	33	35

The sum of the above-named constituents is reckoned as making up 90 per cent of the whole.

A list of all the possible constituents of slags would be a nearly complete list of the metallic elements, together with many of the non-metals. Magnesium and barium may be especially mentioned as constituents which are not unusual, and which at the same time would cause erroneous results if their presence were unsuspected or not provided for. Barium is quite common in lead slags, and is not unknown in iron slags. The reverse may be said of titanium. In general the lead or copper slags contain a greater variety of constituents than do iron slags.

The possible presence in lead slags of small amounts of

lead sulphide, or other easily reducible compounds of fusible metals, renders advisable the addition of a little alkaline nitrate to the flux when such slags are to be fused in platinum crucibles.

Preparing the sample.—By the sudden cooling (chilling) of slag, a material is obtained which when pulverized is readily decomposed by treatment with hydrochloric acid, whereas if they are allowed to cool slowly the same slags cannot be decomposed without resorting to fusion with alkaline carbonates.*

Iles' method of taking the sample is thus described :

“Allow the flowing slag to run upon the end of a steel bar, or dip the bar into the newly-drawn pot of slag; plunge into water, dry the sample upon the slag-pot, powder, and pass through an 80-mesh sieve; now grind a small portion in an agate mortar for two or three minutes, and then weigh out the desired amount for analysis.”

This has been called the “bar method.”

Jones prefers to take the samples by pouring the slag into shallow hemispherical cups in a (cold) cast-iron pan. Others find it more convenient to “granulate” by pouring some of the slag into a bucket of water.

It is usually more convenient to take separate portions of material for different tests rather than to weigh out one portion for *all* of the determinations contemplated. The plan to be pursued when approximate results only are desired may be sketched briefly as follows :

For Silica.—Take 0.5 to 1 gm. Decompose with HCl and evaporate twice. If PbSO_4 is present, dissolve off by supplementary washing with hot strong solution of ammonium acetate or chloride. If BaSO_4 is present, expel SiO_2 by volatilization as SiF_4 , and determine SiO_2 by loss.

Alumina.—In the filtrate from the SiO_2 , precipitate twice

* Chilling applied to lead-silver slags, M. W. Iles, *S. of M. Quarterly*, V., 351; applied to iron slags, Merion and Hart, *J. Anal. App. Chem.*, I., 160; also, C. Jones, *Trans. Am. Inst. Min. Eng.*, XVI., 89.

with ammonia (as described under Limestone). Weigh Fe_2O_3 and Al_2O_3 (possibly also P_2O_5 and TiO_2) together, and deduct Fe_2O_3 (and other constituents) found elsewhere.

Lime.—Precipitate as oxalate in the filtrate from iron and alumina, dissolve in H_2SO_4 , and titrate with standard permanganate.

In the case of the daily examination of lead slags it is not deemed necessary to determine alumina. In that event the filtrate from the silica is rendered alkaline with ammonia, then acid with strong solution of oxalic acid, and, after boiling, the lime is filtered off and determined volumetrically as indicated.

Iron.—Take 0.5 gm. for lead slags, the same amount or more for iron slags, depending upon the content in iron. Decompose with HCl , evaporate off the excess, add a considerable excess of dilute H_2SO_4 , reduce with metallic zinc, and titrate with standard permanganate.

Manganese.—Take 0.5 to 1 gm. Decompose with HCl . Convert to sulphates by evaporation with H_2SO_4 , nearly neutralize, and then titrate with permanganate (see p. 95).

Another method, claimed to be more expeditious, consists in decomposing with HCl , neutralizing with excess of ZnO , digesting with bromine water, and in the precipitate determining the manganese by measuring the oxidizing power of the MnO_2 upon oxalic acid (Williams' method. *Vid.* Manganese Ore).

To describe these operations more in detail: the process briefly mentioned as decomposing with hydrochloric acid is best managed thus: Weigh out, place in a casserole, stir up well with 5 or 6 c. c. of water, then add 5 c. c. of concentrated hydrochloric acid, and a few drops of concentrated nitric acid or a few small crystals of potassium chlorate. Evaporate to dryness on a water-bath, stirring frequently to break up any clots of gelatinous silica which may form. Moisten with about 5 c. c. of water, and evaporate again to complete dryness. Then add again 5 c. c.

of strong hydrochloric acid, heat for a few minutes, dilute to 50 or 60 c. c. and filter, washing as usual.

With blast-furnace cinder (iron slags) it may be better to use more hydrochloric acid (possibly twice as much), and after drying on the water-bath to dry in an air-bath at 120°C . Lead sulphate, if present, may have been partially removed by the treatment with hydrochloric acid. If any remains, it may be dissolved out by treatment with ammonium chloride (acetate, citrate, or tartrate) as suggested. Titanic acid also will only partially remain with the insoluble silica. It tends to hold also some of the Fe_2O_3 , Al_2O_3 , and P_2O_5 in the insoluble portion. Even when titanic acid is *not* present, some Al_2O_3 may remain with the silica. For accurate work, therefore, it is advisable to weigh after ignition, expel the silica by hydrofluoric and sulphuric acids, and weigh again, determining the silica by loss (*vid.* Analysis of Iron Ore).

The residue should be fused with alkaline carbonates, and the solution therefrom added to the main solution. Barium sulphate remains entirely with the silica. Any excess of baryta or of sulphuric acid over and above what will suffice to form BaSO_4 goes into the solution. It may be convenient to add a few drops of sulphuric acid while evaporating in order to have *all* the baryta separated at this place. (Sulphur is determined in a separate portion.)

Addition of a sufficient excess of sulphuric acid so as to drive out *all* hydrochloric acid on evaporating, heating to fumes of sulphuric acid, diluting, etc., in a manner similar to Drown's method (see Manufactured Irons), omitting, however, the washing with hydrochloric acid, gives the advantage of separating all the lead and baryta at this stage of the work, but the complete removal of all the other sulphates by washing is somewhat difficult in many cases.

Dissolving out the barium sulphate with *concentrated* sulphuric acid and filtering through asbestos is a method which may be used to separate it from the silica. The usual method is by hydrofluoric and sulphuric acids, as

just mentioned. To obtain the baryta in the residue, fuse with alkaline carbonates, and extract the alkaline sulphate with water. The residual barium carbonate, probably more or less impure, may then be dissolved in hydrochloric acid, and the barium precipitated by sulphuric acid. The filtrate from this should be added to the main solution if it contains any Fe_2O_3 or Al_2O_3 .

If the slag has not been "chilled," fusion with alkaline carbonate must be resorted to in the manner described (see Feldspar, p. 68). It will be more accurate to conduct the operation for "vitreous silica," *i. e.*, considerable dilution of the water solution from the fusion before acidifying and evaporating down. Of course, after decomposition has been once effected the other manipulations are conducted as for "chilled" samples.

The filtrate from the silica may contain members of the hydrogen sulphide group, which, if not removed by passing the gas through the solution, may interfere with accurate determinations of the other constituents. It must not be forgotten that the use of hydrogen sulphide reduces the iron present to the ferrous form.

Alumina.—It has already been noted that the precipitate produced by ammonia as described may contain many other substances besides Fe_2O_3 and Al_2O_3 . Manganese oxides as well as some others may also accompany the precipitate. The methods described for the determination of Al_2O_3 (Analysis of Iron Ore) should be applied if an accurate result is desired.

In slags from basic processes (Gilchrist—Thomas, etc.) phosphoric acid may be present in considerable amounts, and the slag is valuable on account of its content in phosphoric acid. In such cases the methods described (Fertilizer Analysis) should be used.

Lime.—Manganese and zinc oxalates may accompany the precipitate of calcium oxalate in some measure, if they have not been previously removed. It may, therefore, be necessary to apply the basic acetate separation to the fil-

trate from the silica (or to the filtrate from the hydrogen sulphide treatment after oxidation), separate the manganese by bromine from the filtrate (see Manganese Ore), and the zinc by hydrogen sulphide (see Zinc Ore) before precipitating with oxalate.

In the filtrate from the calcium oxalate magnesia may be determined, if required, by precipitation with hydrodisodic phosphate. In case iron and alumina have not been previously separated, it will be necessary to add about 1 gm. of tartaric acid to prevent the precipitation of those bases along with the magnesium ammonium phosphate.

Iron or Manganese.—For the determination of these constituents separate portions had best be taken as specified. This separation of silica is not essential. The dichromate titration for iron may be used, except when lead is present.

For Sulphur or for Phosphorus.—Take separate portions, using the methods already described (*vid.* Iron Ore, pp. 115 and 116).

For Zinc, Arsenic, Lead, etc., use the methods described under analyses of the respective ores, taking separate portions for each.

CHAPTER XVIII.

MANUFACTURED IRONS.

The possible constituents of manufactured irons are essentially those found in iron ores, and the methods of analysis are very similar. At least two important points of difference, however, must be noted: Manufactured irons often contain carbon in combination, which in the process of solution *may* afford compounds which would interfere with the success of the operations as conducted with ores; also, the constituents usually exist in manufactured irons either in the elemental form or in unoxidized combinations with the iron, and in the case of some (as sulphur and phosphorus), when one adds an acid exerting little or no oxidizing effect, those elements are more or less completely evolved in the escaping gases in combination with hydrogen.

The possible constituents may be thus classified:

Essential.—Iron, Graphite, combined carbon. Usually one or both of the two latter.

Impurities invariably, or almost invariably, present: P, S, Si, Mn, N. The last is seldom determined.

Frequently added for certain purposes: Mn, Al, Cr, Ni, W.

Sometimes present as accidental constituents: Ti, As, Cu, Vd, slag. More rarely other elements may be present.

Sampling.—Especially care is necessary in taking the sample. It should be in the form of chips or drillings bored out of such parts of the pig or bar which will fairly represent the average quality of the material, by a tempered-steel drill used *without oil*. The borer should penetrate nearly through the sample, the borings from the outside being always rejected. Hard samples may be crushed in a steel mortar. In weighing out a sample suitable propor-

tions of both coarse and fine particles must be taken, as there is some difference in composition between those parts which have crumbled to dust under the drill and those which have retained their form. The finer the degree of comminution the better.

Iron.—For the determination of iron, should that be necessary, about 0.5 gm. of the sample will be sufficient. The ordinary method of effecting solution is by the direct use of acid (hydrochloric or sulphuric), though fusion with alkaline carbonate with or without nitrate is sometimes employed, some acid being subsequently used to obtain a solution. Where acid is used directly, it is necessary to add some oxidizing agent to destroy the carbon compounds, which would otherwise interfere with correct results. With nitric acid as the oxidizer, it is not safe to assume that the oxidation is sufficient, unless the solution is evaporated to dryness and the residue heated ("baked") for some little time (20 to 30 minutes at least). Potassium chlorate is more efficient, though not always completely satisfactory. Other methods consist in the addition of solution of potassium permanganate or of dichromate. Hydrochloric acid will be found to be the most efficient solvent, but if it is intended to titrate the solution afterward with permanganate, the amount of this acid remaining in the solution before reducing and titrating the iron should be kept as small as possible. For precautions in titrating in presence of hydrochloric acid see Chapter X.

Carbon.—Up to the present time practically only two forms of carbon are sought in analyzing manufactured irons, viz., graphite and combined carbon. It seems quite probable that irons and steels contain carbon in more than two forms; in other words, that the present classification is too general, and that in the course of time it may become necessary to distinguish those conditions of the carbon more specifically.

A great many methods for the determination of carbon in iron and steel have been proposed and used, of which

only a few can be noticed here. Usually, all that is required to be known is the total amount of carbon. In iron and steel containing no graphite this is all combined.

Where the per cent of carbon present in both conditions (that is, as combined with the iron as carbide and uncombined or graphitic) is required, the total carbon is determined in one portion of the iron, and the graphite in another. The difference between the amount of total carbon, and that of the graphite, gives the amount of combined carbon.

R. E. Rogers and Wm. B. Rogers proposed the use of copper sulphate to dissolve the iron, and the oxidation of the residual carbon by means of potassium bichromate and sulphuric acid, absorbing the resulting carbonic acid in soda-lime or potassium hydrate. (See *Am. Jour. Sci. and Arts*, 1848.)

Ullgren afterward proposed the same method, using chromic acid instead of potassium bichromate. (See *Fres., Quant. Anal.*, 4th London Ed., § 249.)

In a paper published in the *Chemical News* of May, 1869, Arthur Elliott proposed a modification of Rogers's and Ullgren's methods. His process has done good service. It has given very satisfactory results, in a great many analyses, made by the writer, of iron, steel, graphite, and coal of various kinds. For a few experiments, giving the time occupied and the per cent of carbon obtained, by this method, and combustion in oxygen, see a paper published by the writer in the *Am. Chemist* of October, 1871.

Add to 2 or 3 gms. of borings, filings, or very small fragments (in a small beaker) 50 c. c. of a solution of neutral copper sulphate (containing 1 part of the salt in 5 parts of water), and heat gently for about ten minutes. In order to obtain the neutral sulphate, dissolve the recrystallized salt (as sold by the dealers) in water, add a small quantity of copper oxide, boil until the copper sulphate begins to crystallize, filter out the excess of oxide, and

concentrate the solution until it is completely crystallized. Dry the crystals by draining off the water, should there be any, and pressing them between layers of bibulous paper, and dissolve them in water in the proportion stated above. After heating the solution of copper sulphate, containing the iron, about ten minutes, by which means the iron will be dissolved and copper precipitated, add 20 c. c. of a solution of copper chloride (containing 1 part of the salt in 2 parts of water), and 50 c. c. of concentrated hydrochloric acid, and heat to a point just below boiling, with frequent stirring, until the precipitated copper is dissolved, leaving the carbon free. Filter it out through a funnel, made of large glass tubing. The funnel should be about half an inch in diameter, and 5 inches long, and drawn at one end, to a point about 4 mm. wide. Fill the point of the funnel with broken glass, up to the shoulder, and place upon the glass a thin layer of ignited asbestos, pressing it carefully against the walls of the funnel. Care should be taken not to make the plug of asbestos too thick or compact, as it is liable to become clogged by the carbon. The layer of asbestos should be thin enough to allow water to run through at the rate of a funnelful in ten seconds. Transfer the carbon to the filter, and wash with hot water until it is free from chlorides. After washing down all the carbon from the sides of the tube, cut it off about 1 inch above the layer of carbon, by scratching the glass with a file, and pressing a red-hot glass rod against the cut. Then invert the part containing the carbon into the mouth of the decomposing flask of an apparatus similar to that described in the analysis of calcite, for the determination of carbonic acid by direct weight, and blow the contents into the flask, avoiding the use of water by wiping out any carbon that may adhere to the glass with a little ignited asbestos, and throwing this also into the flask. To the filtrate from the carbon add 4 or 5 c. c. of concentrated hydrochloric acid (to prevent the formation of any precipitate of basic copper salt),

and dilute with water, until the fluid is transparent. If any carbon has passed through the asbestos it can readily be seen in the transparent fluid. Should there be any, allow it to settle, filter it out on another filter of ignited asbestos, and add it to that in the flask. Then weigh the absorption-tube, introduce into the flask about 3 gms. of chromic acid, put the apparatus together, and start the aspirator very slowly. After the aspirator has run long enough to partially exhaust the air in the apparatus, introduce, through the funnel-tube, about 30 c. c. of pure concentrated sulphuric acid, close the stop-cock of the funnel-tube, and heat slowly up to boiling. After the acid boils, remove the heat, put on the guard tube, open the stop-cock of the funnel-tube, and aspirate slowly, until the absorption-tube is cool. After it is thoroughly cooled, weigh it, and from the increase of weight, due to carbonic acid, calculate the carbon, (For Elliott's description, consult A. Vacher's 5th Edition of *Fres. Quant. Anal.*, London, 1870.) (See cut on p. 36.)

In most iron laboratories preference is given to methods for burning the carbon to carbon dioxide in a combustion-tube, a current of purified air or oxygen being passed through (often designated as "dry" combustion, in contradistinction to the method above, which has been called "wet" combustion). For separation of the carbon the method with copper sulphate as above may be used, but the use of a double alkali copper chloride has been found more convenient. Until recently ammonium copper chloride has been most generally used, but the recent investigations of the International Standards Committee* have shown that that salt, even when the purest obtainable, is liable to contain some form of carbon, which introduces slight errors. Potassium copper chloride, which can be obtained free from this impurity, has therefore been recommended. Either salt will dissolve the iron, leaving eventually only the carbon. The two stages of the reaction—

* *Am. Inst. Min. Eng.*, xix. 614 and xx. 242.

solution of the iron and subsequent solution of the metallic copper—may often be noted.

For 3 gms. of the sample use 200 c. c. of a solution containing about 380 gms. per litre of pure crystallized potassium copper chloride. A saturated solution of the salt is not so prompt in its action as the above strength. To this amount add about 15 c. c. of strong hydrochloric acid. Keep the solution at about 100° C. (not boiling), with stirring until only carbon remains. Then filter, and wash off all copper salts by the use of hydrochloric acid, and then wash off all hydrochloric acid with hot water. The carbon is then dried (at not too high a heat), placed in a combustion tube, and burned to carbon dioxide, which is caught in potash bulbs and weighed.

The combustion-tubes used are of glass, porcelain, or platinum. Those of porcelain (glazed inside and out) are preferred as being more durable and economical. If a glass or porcelain tube is used, the asbestos filter-bed holding the carbon is placed in a platinum boat of convenient size and shape for slipping it into the tube. The most advantageous arrangement in this respect is to have a boat so constructed that the filtration can be conducted in it. The form recommended by Dudley and Pease ("Proposed Standard Methods," *Jour. Amer. Chem. Soc.*, XV., 501) is three inches long, half an inch wide at top, seven sixteenths wide at bottom, and three eighths of an inch high. It is fitted with a perforated false bottom which leaves a clear space underneath it of about one eighth inch. It also has a tubular opening at one end through which the filtrate runs off. The asbestos used should be previously ignited in a current of air to destroy all carbonaceous compounds which it may contain. The filter-bed is prepared in the same manner as with an ordinary Gooch crucible, flaxing out the asbestos, mixing with water, and pouring the mixture upon the perforated bottom, suction being applied at the same time.

With a platinum combustion-tube is usually supplied a

platinum funnel-tube which slides easily into the combustion-tube.

The use of oxygen for the combustion has but little advantage over air in this operation.

As regards the train for conducting the combustion, Dudley and Pease advise the use of a "preheating" furnace, in which the air used is passed through a tube charged with 8 or 10 inches of granulated copper oxide heated to full redness before it passes through the purifying bulbs or U-tube containing alkali, on its way to the combustion-tube containing the carbon. Purifying bulbs must be used at this point whether a "preheating" tube is attached or not. The purified air (or oxygen) on entering the combustion-tube first encounters the boat containing the asbestos and carbon. Next beyond this is a two-inch roll (moderately close) of silver foil, then a plug of asbestos or some disks of copper gauze, then a few inches of granulated copper oxide, and finally a few disks of copper gauze or an asbestos plug about six inches long.

The ends of the combustion-tubes, both for the "preheating" and the combustion-tube proper, should project well out of the furnaces on either side, to avoid any possible charring of the corks used in making the connections.

Next beyond the combustion-tube comes a bubble-tube or flask about half full of nearly saturated ferrous sulphate solution, acidified with sulphuric acid; next to this another bubble-tube about half full of saturated solution of silver sulphate, acidified, and containing an excess of silver sulphate in suspension. Next a U-tube, loaded with granulated calcium chloride as a dryer; then the absorption bulbs (preferably the Geissler form) containing caustic alkali (best a potassium hydrate solution of sp. gr. 1.27), and connected with a calcium chloride prolong, which is weighed with it before and after the operation; then follows a guard-tube of calcium chloride, and finally an aspirator jar.

All of the connections should be made with glass tubes,

the ends of which abut against one another, short pieces of rubber tubing being used to cover the joints. In this way the danger of error from transpiration of gases through the rubber, etc., can be reduced to a minimum.

The silver foil, ferrous sulphate, and silver sulphate solutions are intended to obviate errors on account of the possible presence of chlorine compounds, which cannot always be certainly removed from the carbon.

The air or oxygen should be supplied from a gas-holder, so lightly weighted that the pressure does not quite suffice to force the gas through the train unless assisted by the aspirator at the other end.

During the operation the gases should pass through the train at the rate of not more than 3 to 5 bubbles per second.

The usual tests should be applied as to tightness of the apparatus before using it, and the precaution of carbonating all calcium hydrate which the calcium chloride may contain must not be neglected.

To insure the absence of impurities in the copper oxide used in the apparatus it is recommended to reduce it in the tubes by heating in a current of hydrogen, and afterward to oxidize up again by heating while passing a current of air or oxygen.

It is well to carry through a blank analysis after everything has been properly arranged and before any analyses are actually made.

In making a combustion the copper oxide in both the "preheating" and in the combustion-tube should be brought to a full red heat before heat is applied to the place where the boat lies. The heat should be made to approach the boat gradually. Of course, whether in heating up or in cooling down, very sudden changes of temperature, which may endanger the safety of the combustion-tube, should be avoided.

The length of time necessary for complete combustion of the carbon (application of a full red heat to the boat) is put

at 15 minutes for steels and 30 minutes for pig-irons. After that, while cooling down, aspirate fully a litre of air through the apparatus.

If a platinum combustion-tube is used, the heat applied should not be greater than will suffice to bring it to a dull-red heat, and the time consumed in the operation must be somewhat longer.

For other methods of conducting the operation see Blair (*Analysis of Iron and Steel*, 2d Edition, pp. 123 *et seq.*). In the method there recommended the products of combustion are first dried by passing through concentrated sulphuric acid, and then through a U-tube containing anhydrous cupric chloride in one limb and anhydrous cupric sulphate in the other, to remove chlorine compounds before passing to the absorption-bulbs. Details as to charging the combustion-tube, the pressure under which the air or oxygen is supplied, etc., are also somewhat different from the above.

GRAPHITE.

The action of acids on manufactured irons affords hydrocarbons by the union of nascent hydrogen with the combined carbon, the graphite being unaffected.

For the determination of the graphite Eggertz's method is as follows: One gramme or more of iron, reduced to small pieces, or white pig-iron crushed in a steel mortar, or gray pig-iron in small chips, is dissolved in 15 c. c. of hydrochloric acid of 1.12 density, in a small flask covered with a watch-glass, and, when the iron is dissolved, the solution boiled for half an hour. All the carbon combined with the iron is disengaged in the form of carburetted hydrogen gas, while the graphite and silica remain. If the carbonaceous residue, left after dissolving the iron, comes in contact with atmospheric air before the liquid is boiled, it is so altered that it is not dissolved, and disengaged as gas. The graphite that remains after boiling the liquid is collected on a filter of known weight, washed, dried, and

weighed. It is then burnt, and the residual silica weighed to ascertain the weight of graphite. See Crookes's *Select Methods*, pp. 79 and 80, where a modification is proposed, as follows :

In a beaker of 100 c. c. capacity, mix 4 c. c. of sulphuric acid and 20 c. c. of water, and when the heat produced by the combination of the water and the acid has entirely disappeared, shake 2 gms. of finely powdered pig-iron into the dilute acid, and boil for half an hour. (For steel and wrought-iron not less than 3 gms. should be taken, and the acid for solution increased in proportion.) The solution is then evaporated until it measures 18 c. c., allowed to cool to the temperature of 50° C., and 4 c. c. of nitric acid of sp. gr. 1.20 added ; boil for a quarter of an hour, and allow to evaporate on a water-bath until, on holding a watch-glass over the beaker, there occurs upon it no perceptible condensation. To the dry mass add 30 c. c. of water, and 5 c. c. of hydrochloric acid, sp. gr. 1.16, boil for a quarter of an hour, and add more hydrochloric acid if there appears to be anything besides silica and graphite undissolved. The insoluble silica and graphite are thrown on a filter (preferably a Gooch crucible, dried at 100° C.), washed with cold water until the washings give no reaction for iron when tested with potassium ferrocyanide, then washed with boiling water containing 5 per cent of nitric acid. The silica and graphite are then dried on the filter at 100° C., and weighed, ignited in a porcelain crucible, and the weight carefully taken. The difference between the weighings before and after ignition gives the amount of the graphite.

The objection to the method of determining the graphite by burning it, after drying it at 100° C., when mixed with silica, is that at that temperature water is not expelled from the silica, or even at a much higher heat. Consequently, the loss which represents the weight of graphite is partly water. This objection applies to all methods where

the graphite is determined by igniting and weighing the residual silica. The extreme difficulty, at times, of burning the graphite in a crucible may be considered another objection.

The best method is to dissolve from 2 to 3 gms. of gray pig-iron, or from 4 to 5 gms. of white iron, steel, or wrought-iron in dilute hydrochloric acid, and boil for about half an hour, filter through asbestos in a funnel made of glass tubing, and arranged as directed for the determination of total carbon; wash with hot water until all acid is washed out, then with strong solution of potassium hydrate, which will remove silica, afterward with hot water, to wash out any potassium carbonate, of which the potassium hydrate is apt to contain some, then with alcohol (which will remove hydrocarbons) until the alcohol runs through the funnel colorless, again with a little hot water, then with ether until it passes through colorless, in order to displace the water, and remove another class of hydrocarbons, which the alcohol may have failed to reach. It is well, finally, to wash with a little hot water (particularly if the ether used is not perfectly pure), in order to keep the graphite from adhering to the walls of the funnel, when blown into the decomposing-flask, being careful to remove any excess of water by gently blowing through the funnel. After the graphite is thoroughly washed, it is transferred to the decomposing-flask, and oxidized with chromic and sulphuric acids, in precisely the same manner as in the determination of total carbon. If it is preferred, the graphite may be transferred to a boat, and burned in a current of oxygen as in Dudley and Pease method (*vid. sup.*).

COMBINED CARBON.

Dr. Eggertz, of the Swedish School of Mines, has proposed a method of determining the combined carbon in iron and steel, by comparing the color of a solution of the iron or steel under examination with that of a solution of another sample of known constitution. When steel or

pig-iron, containing carbon in chemical combination, is dissolved in nitric acid, a soluble brown coloring matter is formed, whose coloring power is very intense, and the solution assumes a tint which is dark in proportion to the quantity of the chemically combined carbon. Iron and graphite do not influence this coloration, for the solution of ferrous nitrate is colorless, or, at most, slightly greenish, unless extremely concentrated, and graphite is insoluble in nitric acid. Thus, in dissolving two pieces of different steels, of the same weight, in nitric acid, taking care to dilute the dark solution until the two liquids present exactly the same color, it is very evident that the more highly carburetted steel will furnish the larger quantity of liquid, and that the proportion of the volumes will indicate the relative proportion of color in the two steels. If, now, the composition and per cent of carbon of one of the steels is known, the absolute percentage of carbon in the other steel may be immediately deduced. Dr. Eggertz has applied these reactions to a method of estimating the combined carbon.

The ways of applying the test are varied almost indefinitely with respect (1) to the amount of the sample taken, (2) the amount of acid used, and (3) the mode of dissolving as regards time and temperature. Whatever may be the conditions produced in these respects, it is imperative that the treatment of standards and samples shall be identical in all particulars. It is also necessary that the standards used (in which the combined carbon has been determined by one of the longer gravimetric processes) should be of the same kind as regards metallurgical and mechanical treatment; *e. g.*, for testing samples of Bessemer ingot, a Bessemer-ingot standard is necessary; for rolled steel, a rolled-steel standard, etc., etc. The percentage composition of the standard should also be approximately the same as that of the samples tested.

(1) Except in the special case of "white iron," when as little as 0.05 gm. may have to be used, the smallest amount

of a sample taken is 0.1 gm., the largest 1.0 gm. 0.2 gm. is the amount taken in many of our steel works, 1 gm. in many others. The larger amount has the advantage of giving a fairer average and less liability to erroneous results from accidental causes.

(2) Nitric acid (gr. 1.2) free from chlorine compounds, nitrous acid, or organic matter, is invariably used as the solvent. Where 0.1 or 0.2 gm. of the sample is used for the test, it is usual to vary the amount of acid taken according to the proportion of combined carbon presumably present; *e. g.* (Blair, *Analysis of Iron and Steel*, 2d Edition, p. 164):

For steels containing C.		Take of nitric acid (Sp. Gr. 1.2).
Under	0.30 per cent.....	3 c. c.
From	0.30 to 0.50 " "	4 c. c.
"	0.50 " 0.80 " "	5 c. c.
"	0.80 " 1.00 " "	6 c. c.
Over	1.00 " "	7 c. c.


Other analysts prescribe somewhat different proportions. Too large a proportion of acid gives paler colors.

When 0.5 or 1 gm. of the sample is taken for the test, the same amount of acid (15 c. c. or 20 c. c.) is (or may be) used irrespective of the probable percentage of combined carbon. There is also a diversity in practice as regards immediate or gradual addition of the amount of acid, addition of the acid to the drillings, or of the drillings to the acid.

(3) The tubes in which the drillings are dissolved are usually immersed in cold water until the first violent action is over. After that they are heated to 80°, 90°, or 100° in a water-bath, or boiled for a definite length of time. Some stop the heating as soon as solution is effected and no more bubbles of gas rise in the liquid; others heat for a certain number of minutes, proportioned to the amount of combined carbon assumed to be present. "Low-carbon steels" require less heating; 20 minutes for low-carbon steels (say

under 0.50 per cent) and 45 minutes for high-carbon steels is a rule adopted by some. Some heat all the samples for a uniform period. Half an hour, one hour, and two hours are periods prescribed by different analysts. The longer periods are only permissible when lots as large as 1 gm. are taken. Long heating causes the colors to become pale. The colors are also faded by strong daylight or by sunlight; the more dilute the solutions, the more rapid the fading. After heating at the temperature and for the period adopted, the solutions should be rapidly cooled by placing the tubes containing them in cold water for a few minutes, when the comparison of the colors can be made.

Comparison may be made *directly* with a solution of the standard which has been made in the same manner and at the same time with those of the samples, or *indirectly* with standard colors prepared by comparison with solutions of the standard, as will be explained later.



For the *direct* comparison it is necessary to have two graduated tubes of exactly the same calibre, made of the same kind of glass, having the proportions of ordinary eudiometer tubes. To facilitate mixing of the contents, the upper (open) end of these tubes should be bent at an angle of about 30° to the axes of the tubes. The solution of the standard is filtered into one tube, that of a sample to be tested into the other, and then one or the other is diluted with cold water until the depth of tint appears the same on looking *across* the tubes toward a sheet of white paper. The relative positions of the tubes should be reversed once or twice before a final decision is reached, since to most eyes the left-hand tube usually *appears* the darker when both are really the same. The amounts of combined carbon in the two samples will then be to one another as the volumes of their solutions.

The colors thus obtained will not, however, keep for more than a few hours. Standard solutions for *indirect*

comparisons are therefore convenient. Such standards may be made with solutions of caramel, from roasted coffee, or of mixtures of ferric, cupric, and cobaltic chlorides diluted so that when placed in a series of tubes of the same calibre each has the depth and quality of tint imparted by a steel or iron containing a certain per cent of combined carbon.

Of organic standards, those made with coffee are the best. Select a good quality of roasted coffee, grind finely, and *digest for some days* cold in alcohol of 50 per cent. Cold digestion is necessary; if heated, the solution will cloud on cooling. Alcohol stronger than 50 per cent dissolves so much resinoid matter from the coffee that it cannot be diluted with water without showing turbidity. If the alcohol is too weak, the solutions will spoil more rapidly by development of mould, etc., and will the more frequently require renewal. Alterations from this cause naturally occur more readily in summer than in winter.

A highly-colored coffee extract having been obtained in the manner suggested, it is filtered and placed in a burette. Another burette is filled with distilled water. Now obtain a solution of the standard steel in the manner to be adopted with all of the samples to be tested, finally making the bulk up to some fixed amount (say 20 c. c.). Run the solution into one of the calibrated tubes, and in another make a mixture of the water and coffee solutions from the burettes which exactly matches the solution of standard steel in depth of tint. Then by a simple calculation the relative amounts of coffee solution and water required to make a series of standard colors can be determined. *E. g.*, suppose the standard steel contains 0.40 of combined carbon; suppose also that 3 c. c. of coffee solution with 20 c. c. of water gives a corresponding color. Then to make 25 c. c. of solution of this shade we would require 3.26 c. c. of coffee solution with 21.74 c. c. water, because $3 : 23 = x : 25$; $x = 3.26$ (coffee), and $25 - 3.26 = 21.74$ (water). Moreover, a solution of one fourth this strength would correspond to

a color obtained by a 0.10-carbon steel ; $3.26 \div 4 = 0.815$ c. c. (coffee) ; $25 - 0.815 = 23.185$ c. c. (water). This is usually called a "ten color." To make a "fifteen color" (0.15 per cent combined carbon) it would require $(1.5 \times 0.815) = 1.22$ c. c. coffee solution diluted to 25 c. c., and so on. It is usually sufficient to make up a series from 0.15 to 0.70, differing from each other by 0.05. Differences of less than 0.05 per cent may be estimated. After making up the color standards the tubes should be well corked and the corks coated with paraffin to prevent evaporation. Thus prepared, these standards, if kept in the dark when not in use, will serve for two months or more without appreciable change. It will be safe, however, to verify them at intervals.

Inorganic standards (which will keep longer) are made by combinations of solutions of ferric, cupric, and cobaltic chlorides. Different analysts use different proportions of these salts and of hydrochloric acid. They agree, however, in preparing first separate solutions of the *neutral* salts, to each of which definite amounts of hydrochloric acid are added in order to prevent the formation of basic compounds, and then mixing these so as to imitate the *quality* of tint obtained from the standard. Then by suitable dilution a set of standards may be made in the manner already described.

By way of example we may cite the proportions given in Blair (*loc. cit.*, p. 168) :

Solution No. 1.	3 gms. Fe_2Cl_6	in 100 c. c. H_2O	with 1.5 c. c. conc. HCl .
" No. 2.	21 " CuCl_2	" " "	0.5 c. c. " "
" No. 3.	2.1 " CoCl_2	" " "	5.0 c. c. " "

A color corresponding to that afforded by 0.2 gm. of a steel containing 1.0 per cent (combined carbon) in 10 c. c. should be obtained by mixing 8 c. c. of No. 1, 3 c. c. of No. 2, 6 c. c. of No. 3, and 5 c. c. of water.

For working by artificial light the standards must be darker than those used by daylight. In some steel works the comparisons are all made by artificial light, in a room

darkened in the daytime. The artificial light may be afforded by kerosene or gas lamps adjusted so as to give a uniform quality and intensity of light. Instead of these some use the monochromatic sodium light.

One mode of applying the test may be described thus : Weigh out 0.2 gm. of each sample to be tested, also of the standard steel. Place each lot in a 4 or 6 inch test-tube immersed in cold water. Add drop by drop the amount of standard nitric acid prescribed according to the amount of combined carbon presumably present. When the first violent action is over, place the tubes in boiling water, or boil cautiously over a naked flame until solution has been effected. Cool by dipping into cold water. Dilute slightly and filter the solutions into graduated comparison tubes, washing the filter with a little cold water. Dilute one or the other until the colors are the same, and calculate the percentage of carbon. Only two comparison tubes will be needed for this test, as the entire set of samples to be tested, if dissolved at the same time, may be compared with the same standard one after the other.

Another method used at the Joliet Iron and Steel Works is thus described by F. A. Emmerton (*Trans. Am. Ins. Min. Eng.*, Oct., 1881, X., 200): "One gram of steel is used for each test, the drillings being put in test-tubes 8 inches long and 1 inch diameter, set in a suitable rack ; 15 c. c. of nitric acid (sp. gr. 1.2) are run into each tube from a pipette, the tubes in the rack being partly immersed in cold water to prevent the reaction being too violent. The tubes are closed loosely with glass bulbs a little larger than the mouth of the tubes, and are set in a water-bath kept at 90° C. for a half-hour. The rack containing the tubes is then set in a pan of cold water to cool the solutions, which in a few minutes are filtered through (dry) 3½-inch filters into a set of test-tubes 5 inches long, and as near as possible ¼ inch diameter. The colors are then compared with a set of standard colors corresponding to every even



hundredth of a per cent, ranging from 0.16 per cent to 0.44 per cent. The standard colors, of course, are kept in tubes of the same size as those into which the solutions to be tested are filtered, and are made from a mixture of the solutions of burnt coffee and caramel in alcohol diluted with its own volume of water, and are found not to vary more than 0.02 per cent in a month. They are renewed generally every three or four weeks, oftener in summer, and less often in winter."

"Tests showing more than 0.44 per cent carbon are made by diluting to half strength with water, and comparing with standard colors, doubling the readings obtained. Tests showing less than 0.16 per cent carbon are made by comparing in graduated comparison tubes with a diluted solution of steel, the percentage of carbon in which has previously been determined by comparison with the standard colors. . . . On account of the length of the tubes in which the solution takes place, and their being stoppered with glass bulbs, loss from evaporation amounts to nothing. . . ."

"Burnt steels" impart a greenish shade to their solutions which is readily recognizable, and gives much difficulty in comparing tints because of a different quality.

When the percentages of carbon are quite low, Stead's alkali method may be used (*Chem. News*, XLIV., 285). That analyst has discovered that the color produced by the action of nitric acid upon steels or irons containing combined carbon is soluble in solution of caustic soda or potash, the alkaline solution having about two and one half times the intensity of the acid solution. The method is also more independent of the class of iron or steel tested. It is carried out as follows: 1 gm. of the steel is placed in a No. 2 beaker, and 12 c. c. of nitric acid (sp. gr. 1.2) added. The beaker is then heated to 90° or 100° C. until solution is effected (usually about 10 minutes); 30 c. c. of hot water are then added, followed by 13 c. c. of caustic soda solution (of sp. gr. 1.27). After thorough mixing,

the solution is poured into a 60-c. c. flask and diluted exactly to the mark, then, after standing for 10 minutes, the solution is filtered through a dry filter, and the color of a definite quantity of the solution (15 c. c. or 20 c. c.) is compared with that obtained from the same amount of solution of a standard steel which has been prepared in precisely the same manner.

Stead notes that a smaller proportion of the soda solution is liable to precipitate the color together with the iron oxide.

To determine the silicon, sulphur, and phosphorus, dissolve 10 gms. of potassium chlorate in 200 c. c. of hot water, in a flask holding at least 1 litre, heat to boiling, and introduce 5 gms. of the iron, in the form of borings or chips. Then remove the source of heat, add (little by little) 60 c. c. of pure concentrated hydrochloric acid, and heat until the iron is dissolved, which may be known by there being no heavy particles on the bottom of the flask, which will not rise when the flask is shaken. There may be a large quantity of black carbon in the fluid, but this will rise when agitated. Transfer the contents of the flask to a large casserole, evaporate to dryness on a water-bath, and then heat in an air-bath, at about 110° C., until the odor of hydrochloric acid cannot be detected. To the thoroughly dry mass add 10 c. c. of hydrochloric acid, and 30 c. c. of water, and heat on a water-bath until everything is dissolved except silica and graphite. Then dilute with 50 or 60 c. c. of water, filter, and wash with cold water, until the washings give no reaction for chlorine. To the filtrate add ammonia in excess, to precipitate the ferric hydrate, which will carry the phosphorus with it, and wash until the washings give no reaction for sulphuric acid. Acidulate the filtrate slightly. With hydrochloric acid, precipitate barium sulphate as usual, and calculate the sulphur. In almost all cases, 2 c. c. of a saturated solution of barium chloride will be sufficient to precipitate all the sulphur in 5 gms. of iron. It

is well, however, to be assured that a sufficient quantity of the reagent has been added, by testing a few drops of the filtrate with sulphuric acid, as directed in the analysis of magnesium sulphate.

To determine the phosphorus, dissolve the precipitate of ferric hydrate, containing ferric phosphate, in pure nitric acid, heat, and proceed as directed in partial analysis of iron ore.

To determine the silicon, dry the residue (containing silica, graphite, and perhaps a little ferric oxide) left after filtering the solution of 5 gms. of iron, burn it in a platinum crucible, add 5 or 6 gms. of sodium carbonate, and 2 or 3 gms. of sodium nitrate, and heat over a good burner until the contents of the crucible are fluid and the graphite oxidized. Do not heat unnecessarily. Treat the fused mass as directed in the analysis of feldspar for the determination of silica. As the silica obtained may contain a little ferric oxide and platinum from the crucible, expel it by means of hydrofluoric and sulphuric acids, and from the loss calculate the silicon. The estimation of the silicon by treating the original residue with hydrofluoric and sulphuric acids, before removing the graphite, would be erroneous, as some of the graphite would also be expelled by the action of the acids. Such has been the experience of the writer.

In most laboratories it is now customary to weigh out separate portions for each determination. In the following some of these methods are described :

Silicon.—Drown's method (*Trans. Am. Inst. Min. Eng.*, VII., 346) is most frequently used. Place in a casserole 1 to 2 gms. of the iron and add 20 c. c. of nitric acid (sp. gr. 1.2). When the first vigorous action is over, add 20 c. c. of diluted sulphuric acid (1:1) and evaporate down to fumes of SO_2 . The nitric acid oxidizes the silicon to silica, which is dehydrated by the concentration of the sulphuric acid. White ferric sulphate separates from the solution ; the material is, however, usually gray from admixture of

carbon. Cool, dilute with about 150 c. c. of water, and warm until the ferric sulphate has apparently all dissolved. Then filter and wash with hot dilute hydrochloric acid until the washings contain no iron, wash with hot water to remove acid, and finally dry, ignite, and weigh. The last portions of ferric sulphate are washed off with difficulty unless the hydrochloric acid is used. For some purposes it may suffice to determine the graphite in the sample by weighing the resulting silica and carbon on a weighed filter, and then burning off the graphite and weighing again. Results obtained in this way, however, can only be regarded as approximate. Some recommend to use the filtrate from the silica and graphite for the determination of other constituents of the iron. This course is not to be recommended, both because the inevitable presence of considerable quantities of sulphuric acid and sulphates in that solution are a source of difficulty in the subsequent manipulations, and because the amounts of iron to be taken so as to give amounts of material that can be conveniently managed are usually too small to be of service in other determinations.

In some cases one encounters highly silicified irons (containing possibly 10 per cent or more of silicon) which yield with difficulty or not at all to nitric acid or aqua regia. Such samples are best decomposed and rendered soluble by fusion with sodium carbonate for 15 to 20 minutes over the blast (Williams, *Trans. Am. Inst. Min. Eng.*, XVII., 542). The melt may be dissolved in dilute hydrochloric acid, and the solution evaporated to dryness as in the case of iron ores.

If for any reason the purity of the silica obtained is open to question, the precipitates after ignition and weighing should be treated with hydrofluoric and sulphuric acids, and the residual impurity weighed and deducted.

Phosphorus.—The methods described under Partial Analysis of Iron Ores ("citric acid method" and "Emmerton's volumetric method") are applicable with such

modifications as the nature of the material demands. Oxidizing agents must be used to convert the phosphorus into orthophosphoric acid, and to destroy the carbon compounds resulting from the decomposition of the iron carbides. Nitric acid is employed as the solvent, but this acid alone will not effect all the oxidation necessary, unless the solution is evaporated to dryness and "baked" for 20 or 30 minutes. The necessity for evaporating to dryness and heating in this manner may be avoided by using solution of potassium dichromate or permanganate and boiling. The latter is usually preferred. Dudley recommends 10 c. c. of a solution containing 12.5 gms. $K_2Mn_2O_8$ per litre, "oxidizing permanganate solution."

If the phosphorus is to be determined gravimetrically, nitric acid (of 1.2) may be used as the solvent, and the solution should be evaporated to dryness to separate silica. (It has, however, been disputed as to whether this is absolutely necessary when the phosphorus is to be weighed as magnesium pyrophosphate.)

When the volumetric determination is to be made, nitric acid of specific gravity 1.135 is preferably used, since that strength of acid does not convert the silica into a form which will clog the filter; and even if some silica accompanies the molybdate precipitate, it causes no error, since no silico-molybdate is obtained (the formation of that compound has been doubted), and the volumetric determination depends only upon the amount of molybdic acid carried down in combination with the phosphorus as phospho-molybdate.

The rapid volumetric method for the determination of phosphorus in iron and steel would be as follows:

1. Treat 1 (or 2) gms. with 60 to 75 c. c. of nitric acid (sp. gr. 1.135) and heat. When the first action is over, boil hard for 1 or 2 minutes.
2. Add 10 c. c. of "oxidizing permanganate solution," and boil until the permanganate color disappears and flocks of manganese oxide appear.

3. Remove from the heat and add ferrous sulphate (free from phosphate), and shake until the manganese oxides are redissolved.

4. Transfer to an Erlenmeyer flask, filtering off graphite if necessary. (With steels the operation may be started in the flask and the filtration dispensed with.)

5. Heat to 85° or 90° C., and add 75 c. c. of molybdate solution.

6. Cork the flask, wrap in a towel, and shake for 5 minutes.

7. Let settle 5 minutes, filter, and wash with acid ammonium sulphate until the washings give no indication of iron or molybdenum when tested with ammonium sulphide.

8. Dissolve the precipitate in 30 c. c. of diluted ammonia (1:4), running the solution at first into the flask in which the precipitation was made, and then again through the filter into a clean beaker. Wash, bringing the bulk up to about 150 c. c.

9. Acidify with 10 c. c. of strong sulphuric acid, and dilute to 200 c. c.

10. Reduce by running the liquid through a "reductor" (see p. 60), washing through with about 200 c. c. more of water.

11. Titrate with standard permanganate, make correction for the reductor, and calculate phosphorus.

It is well to standardize the permanganate by two or three trials on a steel or iron in which phosphorus has been determined gravimetrically. It is usually assumed that the precipitate consists of $12 \text{ MoO}_3 \cdot (\text{NH}_4)_2\text{PO}_4$, and that the molybdic acid in this precipitate is reduced to Mo_2O_3 by the zinc reduction. This would imply that, of a permanganate solution of which 1 c. c. = 0.006141 Fe, 1 c. c. would correspond to 0.0001 P.

In the gravimetric determination, after evaporating to dryness to separate silica, it must be noted that the dried mass dissolves with difficulty or not at all in nitric acid, but is comparatively easily soluble in hydrochloric. It

should therefore be brought into solution by the use of hydrochloric acid, and subsequently evaporated with an excess of nitric acid to a *syrup*, to expel the most or all of the hydrochloric acid before proceeding to the molybdate separation. In diluting up the syrupy solution of ferric nitrate *cold* water should be used, to avoid the troublesome formation of basic nitrates.

In case titanium is present, the phosphorus should be determined gravimetrically, by essentially the same method as described under Iron Ore—Complete.

Sulphur.—A number of methods in use are termed “evolution methods,” because they depend upon the evolution of the sulphur as H_2S when the iron is treated with hydrochloric acid. The gases evolved are passed into solutions in which the hydrogen sulphide is absorbed, and by further treatment the sulphur is determined. The solutions may be those capable of absorbing the hydrogen sulphide as such, or oxidizing solutions. Among the first named may be enumerated that of Karsten with cupric chloride (see *Analysis of Iron and Steel*. Blair, 2d Ed., p. 59), of Morell with ammoniacal cadmium chloride (*Am. Chem.*, III., 180), of Fresenius with ammoniacal silver nitrate (*Quant. Anal.*, Am. Ed., 1883, p. 76), of Forbes with ammoniacal zinc chloride (*Chem. News*, XVI., 105), and of Lippert with potash solution of lead (Fres., *Zts. Anal. Chem.*, II., 46; see also *Ib.*, XIII., 37). The sulphide obtained is in some cases weighed directly after filtering and washing, but is usually oxidized by fusion with alkaline nitrate, and precipitated by barium chloride. Here also belong absorption by potassium hydrate and subsequent oxidation by chlorine (Hamilton; Crookes, *Select Methods*, 1st Ed., p. 84); absorption by potassium hydrate, acidifying, treating with a known amount of standard solution of iodine, and titrating back the excess of iodine by standard hyposulphite (Elliott, *Jour. Lond. Chem. Soc.*, IX., 161); and absorption in a standard solution of iodine in potassium iodide, and titrating the excess of iodine

(Koppmayer; Dingl., *Polyt. Jour.*, CCX., 184). The reaction in the last two cases is $\text{H}_2\text{S} + \text{I}_2 = 2\text{HI} + \text{S}$.

Among oxidizing solutions for the absorption may be mentioned potassium permanganate (Drown, *Am. Chem.*, IV., 42), bromine and hydrochloric acid (Troilius, *Trans. Am. Inst. Min. Eng.*, XII., 509), and hydrogen peroxide (Craig, *Chem. News*, VI., 199). The sulphate obtained is in all cases precipitated in the usual manner with barium chloride.

Here also may be mentioned colorimetric methods, that of Eggertz (Crookes, *Select Methods*, 1st Ed., p. 85) depending upon the quality and intensity of coloration imparted by the escaping gas to a clean strip of silver foil, and Wiborgh's (*Chem. News*, LIV., 158), depending on the depth of tint obtained by passing the gases through a cloth impregnated with solution of cadmium.

One difficulty with the evolution methods is the possible oxidation of the hydrogen sulphide, or of the metallic sulphide, by the presence of air. This may be avoided by conducting the operation in an atmosphere of hydrogen. A more serious objection consists in the fact that with many irons *all* of the sulphur is not evolved as hydrogen sulphide, but remains in the *insoluble portion* in the evolution flask, and consequently has to be sought in two places. This is of frequent occurrence when copper is present, but may occur when it is absent. The insoluble residue in the evolution flask must therefore *always* be examined for sulphur.

Some experiments have made it seem probable that sulphur compounds other than hydrogen sulphide are formed under the conditions obtained, some of which, though not all, are only partially volatile.

Allied to the evolution methods is that of Hibschi (Dingl., *Polyt. Jour.*, CCXXV., 61), in which the drillings are heated in a tube through which a current of chlorine is passed. The sulphur chloride which forms is passed into hydrochloric acid, where it forms sulphuric acid, which is estimated in the usual manner.

Another method, in which the sulphate is precipitated in the presence of little or no iron, is that of Gintl (Dingl., *Polyt. Jour.*, CXCVII., 168). The drillings are treated with ferric chloride. The action may be represented thus: $\text{Fe}_2\text{Cl}_6 + \text{FeS} = 3\text{FeCl}_3 + \text{S}$. The insoluble residue is filtered off, fused with alkaline nitrate, and the sulphate precipitated as usual.

In another series of methods, "precipitation methods," as distinguished from evolution methods, the whole of the sample is oxidized, so as to give the iron in the ferric form in the same solution with the sulphur as sulphate. The oxidizing agent may be bromine water, Nicklès (Fres., *Zts. Anal. Chem.*, II., 438), potassium chlorate (method already described), or nitric acid. The latter is most frequently used. After separation of silica by evaporation the solution is used for the determination of the sulphur. In evaporating care must be exercised not to overheat, and cause loss of SO_3 by dissociation of the iron sulphate. Previous addition of a little sodium carbonate to hold the SO_3 as sodium sulphate is a good device. The difficulties encountered at this point are these: barium sulphate is soluble in hot solutions of ferric chloride; it also has a marked tendency to carry ferric oxide or basic ferric salt with it; if the iron is previously separated by precipitation with ammonia, unless a moderate excess of ammonia is added *at once* (Lunge, *Zts. Angew. Chem.*, 1889, 473), some basic sulphate will accompany the precipitate; and finally, in the filtrate containing ammonia salts, barium sulphate separates in an exceedingly finely divided condition, which gives much trouble in filtering and washing. A plan which is calculated to avoid these difficulties is as follows:*

Weigh out 5.4936 gms. of drillings in a No. 3 beaker, add 60 c. c. of a mixture of one part concentrated hydrochloric acid to fifty parts concentrated nitric acid. Heat

* Communicated by A. L. Colby, Ph.D., of the Bethlehem Iron Works.

gently if the reaction does not begin in the cold, but remove from the source of heat if the reaction takes place too violently, replacing again after action ceases in the cold. If any of the sample resists solution, add 15 or 20 drops of concentrated hydrochloric acid, and continue heating until dissolved. Success in this scheme depends upon care used in this original solution. The beaker should be covered with a clock glass, and every precaution taken to insure thorough oxidation of the sulphur.

When solution is complete, remove the clock glass and evaporate to dryness; when thoroughly dry, add 30 c. c. concentrated hydrochloric acid, and evaporate to dryness again; and when once more thoroughly dry, add 30 c. c. concentrated hydrochloric acid, and boil down to 5 c. c. By this means a thorough separation of the silica and complete removal of the nitric acid is insured.

Next dilute with about 75 c. c. of hot water, and remove carbonaceous residue and silica by filtration, catching the filtrate in a No. 3 beaker. After thorough washing, bring the bulk of the solution up to three fourths the capacity of the beaker by the addition of warm water, and then add 20 c. c. of a just previously boiled solution of barium chloride (1 in 10).

The precipitation is hence effected in a slightly warm solution of such a dilution that it comes down free from iron. The solution is allowed to stand at ordinary temperatures over night, and the next morning the major portion of the clear liquid is siphoned off and not passed through the filter-paper.

The filter is made of two 590 or 589 S. & S. 9 cm. papers, washed several times with very hot water immediately before use.

After filtration the beaker and filter-paper are washed once with hot hydrochloric acid (1 : 1), and finally washed until free from chloride.

Transfer the wet paper with precipitate to a weighed platinum crucible, and after incinerating the paper moisten

with a few drops each of concentrated nitric and sulphuric acids, and re-ignite to convert all to BaSO_4 .

The weight of the precipitate in mgs. divided by 4 and multiplied by 10 gives per cent of sulphur.

Manganese.—For the determination of manganese, the methods described in Chapter XIII. (Manganese mineral) may be used—the chlorate method (Ford's or Ford-Williams), or the Volhard method. The amount of the sample to be taken will depend upon the proportion of manganese presumably present. For *spiegels* (which may contain from 10 to 30 per cent) 0.5 to 1 gm. may be taken. For ferro-manganese not over 0.5 gm. should be used. The procedure is essentially the same as already described. Nitric acid should be used in obtaining the solution; the presence of hydrochloric acid or chlorides is disadvantageous in either method.

With irons or steels containing small amounts of manganese the lead peroxide method may be used. This depends upon the formation of permanganic acid by the action of lead peroxide on a hot solution of manganese nitrate. The method has been used colorimetrically, but is preferably applied as a volumetric method, a standard solution of sodium arsenite being added from a burette until the permanganate color has been discharged. (Deshayes, *Bull. Soc. Chim.*, XXIX., 541.)

A convenient quantity of the sample (0.1, 0.2, or 0.5 gm.) is boiled in a test-tube or small beaker with 15 to 30 c. c. of nitric acid (sp. gr. 1.2) until all nitrous fumes are gone. Then dilute with an equal bulk of hot water, and boil. While boiling add lead peroxide (PbO_2) or red lead (Pb_3O_4) in the proportion of about 1 gm. of the oxide to every 2 mgs. of manganese presumably present. Boil for at least three minutes after addition of the lead oxide. Filter through asbestos, washing by decantation with hot water containing about two per cent of nitric acid (containing no nitrous acid), boiling up after each addition of the wash-

water. Titrate the filtrate with a solution of sodium arsenite.

The sodium arsenite solution is made by dissolving 5 gms. of arsenious oxide in a boiling solution of 10 to 15 gms. of sodium carbonate, cooling and diluting to two litres. It is best standardized by use of weighed quantities of a steel containing amounts of manganese accurately determined by gravimetric methods.

The asbestos used in filtering should previously be tested to be certain that it exerts no reducing action upon the solutions.

Aluminum.—Within the past few years the addition of aluminum to irons has been found to be attended with certain advantages, and the determination of that element has become necessary in many cases. The methods used have been chiefly those depending on the precipitation of the alumina as phosphate in a solution where the iron has been reduced to the ferrous form by hyposulphite, the other conditions being essentially such as are produced in effecting the basic acetate separation. (Stead, *Jour. S. C. Ind.*, VIII., 966; Phillips, *Chem. News*, LXI., 313; Carnot, *Bull. Soc. Chim.*, [3] V., 139.) Carnot's method is as follows: Dissolve 10 gms. of the sample in hydrochloric acid, filter into a flask, wash the residue well, nearly neutralize with ammonia and sodium carbonate, and add concentrated solution of sodium hyposulphite. When the tint has passed through violet to colorless, add 2 or 3 c. c. of a saturated solution of sodium phosphate and 5 or 6 gms. of sodium acetate. Boil until no odor of sulphurous acid is perceptible. Filter and wash the precipitate of impure alumina phosphate. Dissolve in hydrochloric acid, and evaporate to dryness to separate silica. Dissolve in hydrochloric acid, filter, and treat the solution as before, using about 2 gms. of sodium hyposulphite and 2 gms. sodium acetate. Ignite and weigh the last precipitate as $\text{Al}_2(\text{PO}_4)_3$, and calculate aluminum.

Drown and McKenna, *Trans. Am. Inst. Min Eng*

June, 1891) have recommended a method which consists in separating the iron electrolytically and then precipitating the alumina as phosphate. In this method 5 to 10 gms. of the sample are dissolved in sulphuric acid and the solution is evaporated to fumes; after dilution and filtration the solution is nearly neutralized with ammonia, and then subjected to electrolysis for 10 to 15 hours, the solution being made up to 300 or 500 c. c., and standing over mercury connected with the cathode. The mercury should weigh about 100 times as much as the iron taken for analysis. A current of about two amperes is necessary. When the solution gives no reaction for iron, remove it and wash before breaking the circuit. To the solution and washings add an excess of sodium phosphate and about 10 gms. sodium acetate, nearly neutralize with ammonia, and boil for at least 40 minutes. The precipitate consists apparently of $7\text{Al}_2\text{O}_3$, $6\text{P}_2\text{O}_5$, containing 24.14 per cent aluminum. If it is colored with iron it must be brought into solution by fusion with potassium bisulphate, and the electrolytical separation, etc., repeated.

Chromium.—Dissolve 2 to 5 gms. in sulphuric acid (1:2) by the aid of heat, and filter. Render the solution alkaline with sodium carbonate, and add bromine water to oxidize the iron, chromium, and manganese, keeping the solution alkaline by addition of more sodium carbonate solution if necessary. If manganese is present the solution will assume the color of alkaline permanganate. If only chromium is present the yellow of sodium chromate will be perceptible. Filter, wash, and treat the precipitate a second time with dilute sodium carbonate and bromine water, to be sure of obtaining all of the chromium. If the solution shows no color, all of the chromium is in the first filtrate. Add ammonium nitrate in excess, and evaporate the solution; if manganese is present, the permanganate will oxidize the nitrogen of the ammonia, affording insoluble hydrated manganese dioxide and alkaline nitrate. Continue the evaporation to dryness, moisten with nitric acid and dry

again, take up with dilute nitric acid, and filter. In the filtrate reduce the chromium by sulphurous acid, and precipitate with ammonia as in the analysis of chromite. The precipitate must be redissolved and reprecipitated twice or more in order to obtain pure Cr_2O_3 .

Nickel.—Dissolve in nitric acid, evaporate to dryness and heat some time, then take up with strong hydrochloric acid and filter. The methods for separating the iron, and subsequently the nickel, are essentially the same as those described under nickel ore (Chapter XXI.). The method recommended by Blair (*Analysis of Iron and Steel*, 2d Ed., p. 178) consists in precipitating the iron two or three times as basic acetate, and in the combined filtrates separating the nickel (and possibly cobalt) as sulphide. The methods for separating cobalt and determination of the nickel are described under analysis of nickel ore (*loc. cit.*).

Tungsten is also added to certain irons and steels to impart certain desirable qualities for special purposes. To determine this element dissolve 5 gms. of the sample in nitric acid (sp. gr. 1.2) as for phosphorus (in Emmerton's volumetric method), and heat for about 30 minutes to effect complete oxidation of the carbon, etc. Then add 40 c. c. of hydrochloric acid, and digest warm for some time. The insoluble residue will consist of tungstic acid, silicic acid, and some impurities. Filter and ignite this residue. Expel the silica by hydrofluoric and sulphuric acids in the usual manner. The tungstic acid (which is eventually weighed as such) may be extracted by ammonia or by fusion with sodium carbonate. In using the first method digest warm with ammonia for an hour or more, adding ammonia from time to time, so that the solution always smells strongly of NH_3 ; filter, and wash with ammonia water. Heat the filtrate with potassic hydrate until ammonia is expelled, filter if necessary, and then acidify with hydrochloric acid, and digest until the tungstic acid is completely precipitated. Filter, wash, ignite, and weigh.

In the other method fuse the residue freed from silica with about three times its weight of sodium carbonate, and after cooling, extract with hot water, filter, and wash with water containing a little sodium carbonate. Boil the filtrate, adding nitric acid cautiously until the carbonate is nearly all decomposed and the carbonic acid expelled, keeping the solution still slightly alkaline. Then render the hot solution slightly acid with nitric acid, and add mercurous nitrate, and a little mercuric oxide suspended in water to neutralize the free acid. Let stand until the precipitate separates readily, filter off the mercurous tungstate, and wash with hot water; ignite to tungstic acid (WO_3), and weigh.

Nitrogen may be determined by Langley's modification of A. H. Allen's method *Chem. News*, XLI., 231 (*vid. Blair, Analysis of Iron and Steel*, 2d Ed., p. 195).

Titanium (and phosphorus when titanium is present).—Dissolve 5 gms. in 60 c. c. of nitric acid (sp. gr. 1.2), evaporate to dryness, and heat 30 minutes. Add 40 c. c. strong hydrochloric acid and heat until solution has been effected. Dilute and filter, disregarding the opalescent cloudiness of the filtrate which is liable to appear. Dry the filter, burn off paper and graphite in a platinum crucible, and treat the residue with hydrofluoric and sulphuric acids to remove silica. Meantime precipitate the hydrochloric acid solution by addition of sodium carbonate, filter off the precipitate, dry it, pulverize, and mix with 20 gms. dry sodium carbonate; place the mixture in the crucible containing the residue from which silica has been expelled, and fuse the whole for at least an hour over a good burner. Cool the melt, boil with water, and filter. Wash until the washings begin to run turbid, then dry the material insoluble in water, mix with more sodium carbonate, and fuse, etc., as before. Test the water solution from the second fusion for phosphoric acid by acidifying with nitric acid and addition of molybdate mixture. If little or no precipitate is obtained a third fusion will be unnecessary.

The water solutions from the fusions contain the phosphoric acid which may be separated with molybdate solution, etc., in the usual manner, while the residue insoluble in water contains the titanium as sodium titanate mixed with ferric oxide. Treat as directed in complete analysis of iron ore (pp. 127 *et seq.*).

Arsenic.—Dissolve 5 to 10 gms. in hydrochloric acid with aid of potassium chlorate, evaporate off all free chlorine, and filter. If hydrochloric acid alone is used some arsenic may be lost as arsine, or, if the acid is concentrated, as arsenious chloride. Filter off graphite, etc., and saturate with hydrogen sulphide. The precipitation of the arsenic may be assisted by heating, most advantageously by applying heat to a corked-up bottle containing the solution as described under Arsenic Ore. Filter and wash the precipitate. When free from all hydrogen sulphide treat with warm solution of ammonium carbonate which dissolves arsenic pentasulphide. On acidifying this solution with hydrochloric acid the pentasulphide is reprecipitated, when it may be filtered on a weighed filter, washed, dried, and weighed.

Lundin's distillation method (*Chem. News*, LI., 115), which is practically only an adaptation of Fischer's method for arsenic ores (which see), may also be used. Dissolve 6 gms. or more of the sample in 70 c. c. of nitric acid (sp. gr. 1.2), add sulphuric acid, and evaporate to fumes. Heat for some little time to insure the complete expulsion of the nitric acid. Transfer to a flask of about 300 c. c. capacity, add about 10 gms. of pulverized ferrous sulphate and 70 c. c. of strong hydrochloric acid, and distil off AsCl_3 . The distillation flask is fitted with a cork carrying a tube bent twice at right angles, the end of which is joined to a 50 c. c. pipette, the tip of which dips below the surface of water in a beaker. When the bulb of the pipette begins to grow warm, it may be assumed that all of the arsenic has been distilled over. Disconnect, rinse out the pipette, and precipitate the distillate with hydrogen sulphide. The

arsenious sulphide may be dried and weighed as such, or it may be fused with sodium carbonate and nitrate, and the arsenic determined by Pearce's method (see arsenic ore).

Copper may be found in the sulphide precipitate, in the portion left insoluble in ammonium carbonate solution, when arsenic has been sought in the manner first described. If copper only is sought, time may be saved by dissolving 5 to 10 gms. of the sample in strong hydrochloric acid, distilling, filtering, adding about 10 gms. of sodium hyposulphite, and boiling. Under these conditions the copper is precipitated as Cu_2S . In either case the sulphide, after filtering and washing, is roasted to convert to oxide, and to remove arsenic and sulphur. The oxide is then dissolved in a little nitric acid and electrolyzed after addition of sulphuric acid, or the copper may be determined by some of the other methods given under copper ores.

Vanadium.—Dissolve 5 to 10 gms. in 70 to 80 c. c. of nitric acid, evaporate to dryness in a platinum dish, and heat for some time. Pulverize the residue, and fuse with 25 gms. of dry sodium carbonate and 3 gms. of sodium nitrate, maintaining a high temperature with the aid of the blast for some time.

Cool the melt, boil with water, and filter. To the filtrate add nitric acid and boil to expel carbon dioxide, keeping the solution faintly alkaline. A yellow color in the solution when it is acid is indicative of the presence of vanadium. Remove from the source of heat, acidify slightly, and precipitate by addition of mercurous nitrate, neutralizing with mercurous oxide as in the case of tungsten. Filter off the precipitate, ignite to expel mercury compounds, and fuse the residue with a little sodium carbonate. Dissolve in a little water, filter if necessary, render alkaline with ammonia, and add solid ammonium chloride in sufficient quantity to saturate the solution (nearly 4 gms. for every 10 c. c.). Allow to stand for some time, keeping the solution alkaline with ammonia throughout. White

ammonium vanadate separates, which may be filtered off, washed with strong ammonium chloride solution, and then cautiously ignited to V_2O_5 and weighed.

To determine any slag that may be mixed with cast-iron, pulverize about 3 gms. as finely as possible by boring with a dull drill and rubbing in a steel mortar, being careful not to lose any of the dust. Add this (little at a time) to 6 c. c. of bromine, previously mixed with 60 c. c. of water which has been boiled and cooled to 0°C . in a beaker of about 100 c. c. capacity. Keep the fluid at 0°C . for 3 hours, with frequent stirring. No evolution of gas should take place. After the iron appears to have dissolved, allow the fluid to stand for 24 hours at the ordinary temperature of the atmosphere. Then add 30 c. c. of ice-water, which has been previously boiled, allow the mixture to settle, and decant, on a small filter, the fluid containing light particles of carbon. Repeat, until only hard, dark powder remains at the bottom of the beaker. Test this for undissolved iron, by adding 2 drops of hydrochloric acid, and 5 c. c. of water. If any iron be present, gas will be evolved. Whether iron be present or not, decant immediately on the filter, and wash, to avoid affecting the slag. If the hydrochloric acid has shown the presence of iron, add 30 c. c. of ice-cold water, which has been previously boiled, and 3 c. c. of bromine, and proceed as in the first instance, in order to dissolve all iron. Filter, and wash with cold water, until the washings give no reaction for iron. Dry the filter and contents, ignite, transfer the ignited substance to a silver or platinum dish, add solution of pure sodium hydrate, and digest, to dissolve free silica. Then filter, wash well, dry, ignite, cool, and weigh the slag. Iodine may be used instead of bromine. If iodine be used, add the same quantity of iron, reduced to as fine a powder as possible, to 15 gms. of iodine, covered with 15 c. c. of water, in a beaker of about 100 c. c. capacity, the water having been boiled previously to remove any air adhering to the iodine, and cooled by stand-

ing in ice. After adding the iron, proceed as when bromine is used.

Consult Fres., *Zeits. für Anal. Chem.*, 1865, pp. 69-77; *Wag., Jahresb.*, 1863, p. 19; same, 1865, p. 27; same, 1868, p. 28; *Comp. Rend.* 2, p. 1030; Dingler, clxxvii., p. 388; Eggertz, *Jahresb.*, 1863, p. 30; Blair, *Analysis of Iron and Steel*, 2d Ed.; Troilius, *Notes on the Chemistry of Iron, Steel*, etc.; also *Transactions Am. Inst. Min. Eng.*, Vols. X. *et seq.*

CHAPTER XIX.

ALUMINUM AND ALUMINUM BRONZE.

With regard to the choice of solvents it may be stated in general terms that hydrochloric acid attacks aluminum most readily, whereas nitric acid is most efficient in dissolving copper, which is almost invariably present in commercial aluminum, as well as in aluminum bronzes. Hence the proportions of those acids to be used will depend upon the relative proportion of aluminum present. 10 c. c. of concentrated hydrochloric acid (diluted with two or three times its bulk of water to moderate the vigor of the reaction) will suffice to dissolve one gramme of aluminum, and it may be assumed that about 5 c. c. of nitric acid (sp. gr. 1.2) is sufficient to dissolve one gramme each of the metals with which it is likely to be associated. A good plan to pursue is to treat the metal or alloy with 10 c. c. of concentrated hydrochloric acid (suitably diluted) for each gramme taken, and then to heat, adding from time to time a little nitric acid as it may be found necessary to maintain an active solvent action. With commercial aluminum it is always advisable to add at least a few drops of nitric acid toward the end.

On evaporating to dryness it will be found that the portion thus rendered insoluble is a mixture of silicon and silica, together with possibly some other substances. To obtain the silica, filter off, wash, dry, and ignite this residue to ash in a platinum dish. Then fuse with about five times its weight of mixed sodium and potassium carbonates, which converts all the silicon into silica. Cool the melt, dissolve *completely* in water, then acidify with hydrochloric acid, and evaporate to dryness in the usual manner for the determination of silica. Treating with hydrochloric acid and water, and evaporating a second

time at this stage, contributes to the accuracy of the determination. Wash, dry, ignite, and weigh the silica with the usual precautions, adding the filtrate and washings to the first filtrate. In this solution (divided if necessary into aliquot portions) the copper and aluminum may be determined.

For the copper add sulphuric acid, evaporate to fumes, dilute, and determine by electrolysis.

If it is desired to determine the aluminum, saturate the solution with hydrogen sulphide to remove the copper, and to the filtrate from this add ammonia in slight excess, and boil, adding a little ammonium sulphide should it be necessary to preserve a slight excess of that compound in the solution. Aluminum hydrate cannot be precipitated pure in presence of copper. The use of ammonium sulphide helps to prevent the presence of basic aluminum chlorides in the precipitate. The precipitate should be washed repeatedly by decantation, boiling up each time with water. Under these conditions, iron, in the form of sulphide, accompanies the alumina, but will be converted to Fe_2O_3 , on igniting the precipitate after moistening with a little nitric acid. The amount can be determined in another portion of the sample by methods to be described. After thorough washing of the precipitate, dry and ignite strongly. After weighing, test it by warming for some time with nitric acid in which it should be insoluble. The nitric acid from this digestion should give no precipitate of alumina with ammonia or any turbidity with silver nitrate (chloride).

In aluminum bronzes the proportion of iron is usually very small, and titration of the same is practically impossible in presence of so much copper. In such cases, dissolve up 2 to 3 gms. of the alloy, add to the solution 6 to 8 gms. of tartaric acid (free from iron) for every gramme of aluminum assumed to be present, and precipitate out the copper by hydrogen sulphide. To the filtrate add ammonia in slight excess, which should precipitate ferrous sulphide

free from alumina if enough tartaric acid has been added. The addition of a little ammonium sulphide may sometimes be necessary, but ordinarily the filtrate contains enough hydrogen sulphide to precipitate all the iron. Filter, wash with dilute ammonium sulphide, and dissolve in hot dilute sulphuric acid. Boil, reduce with zinc, and titrate with standard permanganate of one tenth the strength of that ordinarily employed.

With commercial aluminum the copper is too small in amount to interfere on account of its color, and a solution obtained as described *after separating the silica* may be evaporated with sulphuric acid, reduced, and titrated in the same manner. Titration of the first solution from the sample, containing, as it usually does, silicon and possibly some oxidizable carbon compounds, will not afford correct results.

With commercial aluminum the residue left insoluble on treating the metal with caustic soda or potash solution contains all of the copper, and in many cases all of the iron also. A convenient strength for the solvent is 200 gms. of the caustic alkali per litre of water, of which 30 or 40 c. c. is used for every gramme of metal. After solution has been effected, dilute with about three volumes of water, and pass a current of air, or add a little hydrogen peroxide, when manganese, and possibly some other constituents, will separate in the insoluble form. Filter and wash, dry and incinerate the filter-paper, and fuse the residue with mixed alkaline carbonates, adding a few fragments of potassium nitrate at the end of the fusion to oxidize the carbon (probably graphitic) from the sample. Dissolve the melt in hydrochloric acid (which is the only acid giving readily a complete solution) and use the solution for the determination of copper, manganese, and iron. As regards testing for the latter, the absence of iron in the caustic-alkali solution must be assured.

For that purpose pour the alkali solution slowly into an excess of hot dilute acid, stirring vigorously all the

time. If the reverse method is used—adding acid to the alkali—a voluminous precipitate of alumina hydrate mixed with basic salt will form, which is brought into solution with some difficulty. In the acid solution test for iron by sulphocyanate. If any appears, the tartaric-acid method must be used for the estimation of the iron.

According to Hunt, Clapp, and Handy (*Jour. Anal. and App. Chem.*, VI., 24) the portion insoluble in caustic alkali also contains the titanium and chromium which are often added to impart hardness.

To determine chromium they recommend that, after filtering off, the insoluble portion (after burning off the filter-paper) be treated with sulphuric and hydrofluoric acid, heated until only sulphuric fumes are evolved, and then fused with potassium bisulphate, the temperature being raised toward the last so as to bring the flux nearly to the neutral condition. Sodium carbonate and potassium nitrate are then added, and the mass fused again, which affords alkaline chromate. Cool, dissolve in water, filter, add ammonium chloride, and heat to separate silica and alumina, and in the filtrate from these reduce and precipitate the chromium as directed under Analysis of Chromite.

To determine titanium the metal (2 gms.) is dissolved in caustic alkali as before, and the residue fused with potassium bisulphate in a similar manner, except that a larger amount of bisulphate is used (6 to 8 gms.) added by installments, and the fusion is more prolonged (about 30 minutes). Finally 2 gms. of the bisulphate is added, and the mass is just brought to full fusion, avoiding the expulsion of much of the sulphuric acid. Cool, dissolve out with lukewarm water, filter, just neutralize the solution with ammonia, render slightly acid with sulphuric acid, and then add sulphurous acid and boil for 45 minutes, adding sulphurous acid from time to time, to keep the iron in the ferrous condition. Filter and weigh the precipitate of TiO_2 . The addition of a little sodium acetate will assist the separation of the titanium.

CHAPTER XX.

ZINC ORE.

Make a qualitative examination of the ore, for metals of Groups V. and VI.

Treat 2 gms. of the finely pulverized ore, in a small flask, with aqua regia—about 5 c. c. of hydrochloric and 2 c. c. of nitric acid; heat to effect decomposition, and then add about 5 c. c. sulphuric acid. Boil until copious fumes of SO_2 are evolved, cool, dilute with 25 c. c. of water, filter, and wash well. If the qualitative analysis has shown the presence of oxides of the higher groups, add 5 c. c. of hydrochloric acid, and saturate the solution, which should not exceed 500 c. c., with sulphuretted hydrogen. Filter, wash slightly, digest the precipitate with a mixture of 5 c. c. of hydrochloric acid, and 10 c. c. of water over heat, dilute to about 400 c. c., and, without filtering, saturate with sulphuretted hydrogen. (See Fres., *Quant. Anal.*, § 162—A.) Filter, wash well with hot water, combine the filtrates, and boil, after adding a little potassium chlorate to oxidize the sulphur, and precipitate basic acetates as usual. If no metals of the higher groups be present, the treatment with sulphuretted hydrogen and potassium chlorate is to be omitted. In either case, filter out the precipitate of basic acetates, dissolve it in hydrochloric acid, dilute, and precipitate again in the same way. Filter, dissolve the precipitate as before, and precipitate, a third time, with large excess of ammonia, filter, and wash. Combine all the filtrates, concentrate them to 500 c. c., add about 5 c. c. of acetic acid, boil, and, while boiling, pass a rapid current of sulphuretted hydrogen for half an hour. By this means the zinc will be precipitated as sulphide, and the manganese be held in

solution. (See Fres., *Quant. Anal.*, § 160—6—a; also Gibbs, in *Am. Jour. Sci. and Arts*, January 7, 1868.) If there be a very large amount of manganese in the ore, it is well to dissolve the zinc sulphide in hydrochloric acid; make the solution slightly alkaline with sodium carbonate, and then decidedly acid with acetic acid, boil, and treat with sulphuretted hydrogen as before, as the zinc may carry down some manganese with it. Filter out the zinc sulphide, wash it by decantation 2 or 3 times with hot water, and then, on the filter, with sulphuretted hydrogen water, into small beakers, changing them often, in order not to be compelled to refilter a large amount of fluid, should the zinc sulphide run through the filter, which it is apt to do, as soon as the ammonium chloride is washed out. Usually the precipitate is sufficiently washed when the washings begin to run turbid. Transfer the most of the precipitate, by means of a spatula, to the beaker in which the precipitation was made, place that beneath the filter, and run through enough hot dilute nitric acid to dissolve off the adhering precipitate. Use a little more acid, if necessary, to bring the whole into solution. Boil to granulate the sulphur which separates and to expel hydrogen sulphide, and then filter. From this solution, which should have a bulk of about 200 c. c., the zinc may be separated as basic carbonate (weighed as ZnO) or as zinc ammonium phosphate (weighed as $\text{Zn}_3\text{P}_2\text{O}_8$).

For the first, add to the hot solution sodium carbonate in slight excess, and boil for a few minutes. Then withdraw the heat, allow the precipitate to settle, and wash several times with hot water (at first by decantation) until the wash-water shows no alkalinity. Dry, remove the precipitate from the paper as much as possible, moisten the paper (in a weighed crucible) with solution of ammonium nitrate, dry and incinerate, then add the precipitate and heat slowly up to intense ignition. Cool and weigh. The chief objection to this method is the difficulty in completely washing the sodium carbonate from the precipitate.

Always test the filtrate with hydrogen sulphide to make sure that all the zinc has been precipitated.

For the phosphate method (which is preferable) add to the acid solution three times the calculated amount of phosphorus salt (about 6 c. c. of a cold saturated solution for every 0.1 gm. of zinc assumed to be present). This excess is needed to render the precipitate sufficiently insoluble. Heat for about 5 minutes, and then add ammonia little by little, until the solution is just alkaline. Heat on the water-bath until the precipitate becomes crystalline-granular, and settles readily and the odor of ammonia is gone. Boiling is impracticable, as the solution "bumps" dangerously. Wash by decantation, pouring the solution and washings through a small filter; finally dissolve the precipitate in a little nitric acid, running the solution through the filter into a small weighed capsule. Evaporate to dryness, and heat up gently at first, finally to full redness. Cool and weigh. By this means the reduction of the zinc compound to volatile metal by the burning filter-paper is avoided.

Drying the ZnNH_4PO_4 on a tared filter at 100°C . and weighing it as such, is sometimes practised.

Test the filtrate with hydrogen sulphide for zinc, as directed in the other case.

Of volumetric methods for zinc, but two require consideration—sodium sulphide, and potassium ferrocyanide. The objections raised by many analysts to either of these methods are, that much labor is involved in preparing the solutions to be titrated, and, moreover, that the management of the titrations are attended with more or less troublesome manipulation. Manganese especially, a frequent constituent of zinc ores, is separated from the zinc with difficulty, and, if allowed to remain in the solution, will react with either of the above reagents, and consequently be estimated as so much zinc.

The *sodium sulphide* titration is usually made with a solution of Na_2S of such strength that 1 c. c. = 0.008 to

0.010 gm. of metallic zinc. The zinc solution should be alkaline with ammonia. The "end-reaction" is when a drop of the clear solution after vigorous stirring just shows a brown tint upon paper saturated with solution of lead acetate. Paper or cards covered with a lead glaze have been found convenient for this purpose. Other methods of detecting the presence of soluble sulphide may be used. A serious objection to this method consists in the rapid deterioration of the test solution, which consequently requires frequent re-standardization.

Ferrocyanide titration.—A convenient strength for the test solution is 44 grammes pure crystallized potassium ferrocyanide per litre; 1 c. c. = about 0.010 gm. Zn.

The titration is usually performed in a hot solution, acid with hydrochloric acid, and containing ammonium chloride. Lead, if present, will interfere with the accuracy of the titration, unless the solution contains some free acid. As an indefinite excess of acid produces irregular results, it is best to add to the solution a few drops of methyl orange indicator as a guide, then to neutralize, and after that to add a definite excess of hydrochloric acid (1 c. c. of concentrated acid to about 200 c. c. of the solution) before proceeding with the titration. The end-reaction is when a drop of the solution, brought in contact with a drop of saturated solution of uranium acetate on a porcelain plate, gives the brown tint of uranium ferrocyanide.

Either the sulphide or ferrocyanide solution should be standardized by the use of a solution made by dissolving a known amount of metallic zinc or of *pure* zinc oxide, the conditions produced for titration being essentially the same as those obtained with the solutions from ores, etc., as to amount of zinc, amount of ammonium chloride, bulk and temperature of the solution, degree of alkalinity or acidity, etc. A correction of the burette reading for the amount of test solution necessary to produce the end-reaction when no zinc is present should also be determined.

A. H. Low (to whom some of the suggestions in the pre-

ceding paragraphs are due) has devised a method by which a solution of the zinc in ores can be obtained free from manganese and other disturbing elements (except cadmium) (*Colorado Sci. Soc.*, June, 1892). His method was intended for application to ores used in lead smelting, but with some modifications may be made applicable to zinc ores in general. The main feature is the separation of manganese as a higher oxide by potassium chlorate in a nitric acid solution.

As modified so as to be applicable to zinc ores in general, the method would be as follows (see paper by B. C. Hinman, *S. of M. Quarterly*, XIV. 40):

Attack 1 to 2 gms. of the finely pulverized ore in a small casserole with 5 c. c. concentrated hydrochloric and 5 c. c. concentrated nitric acids, and evaporate off the excess of acid. In the case of some Franklinites, and possibly others, it will be necessary to dilute, filter, and fuse the insoluble residue with a couple of grammes of sodium carbonate, to render all of the zinc soluble. In such cases dissolve the fused mass in nitric acid, and add to the main solution. In either case, add 5 c. c. of strong nitric acid, and evaporate to dryness, avoiding overheating and baking. The object of the evaporation is to complete the solution of the zinc, to granulate the silica, and to convert the remaining chlorides into nitrates. Then add about 20 c. c. of a saturated solution of potassium chlorate in nitric acid, and evaporate again. Some easily decomposable ores may be treated immediately with the chlorate solution, the aqua regia treatment being omitted.

Cool the casserole, add 7 gms. of ammonium chloride, about 15 c. c. of strong ammonia and 25 c. c. of hot water; by means of a rubber-tipped rod, detach all particles adhering to the casserole. Then boil for a minute or two, and filter, washing with a hot 10 per cent solution of ammonium chloride. If the ore contains much iron, some zinc may be retained by the ferric oxide and hydrate. In such a case, rinse the contents of the filter back into the

casserole with dilute nitric acid and boil down with some chlorate mixture as before, taking up again with ammonium chloride, etc. A third treatment may be sometimes advisable.

Unite the filtrates and washings (which should be brought to a bulk of about 200 c. c.), add a few drops of methyl orange indicator, neutralize, then add 1 c. c. of concentrated hydrochloric acid, and titrate hot with the standard ferrocyanide.*

If the solution contains undecomposed chlorate the methyl orange will be bleached when free acid is added. Should that occur, destroy the chlorate by addition of a few drops of ammonium bisulphite to the acid solution, boil out excess of sulphurous acid, and proceed.

If the ammoniacal solution is blue from the presence of copper, remove that element by adding 10 to 40 gms. of granulated (test) lead to the acidified solution, and stir until it is absolutely colorless; then, without filtering, neutralize and proceed at once to the titration.

* If the zinc solution is kept at boiling temperature, a sharp end-reaction can be obtained by allowing a drop of the *hot* solution to fall on a drop of strong solution of platinic chloride on a white plate. The least trace of ferrocyanide in the solution will cause the development of a green coloration. If the zinc solution is cold, this reaction will be slow and unsatisfactory.

CHAPTER XXI.

NICKEL ORE.

Nickel ores usually contain arsenic, and very frequently other members of the hydrogen sulphide group. The chief difficulty encountered is that of separating completely the iron present from the nickel (and cobalt) in order that the latter may be determined. Both the basic acetate and ammonia precipitates retain nickel, which can only be recovered by repeated resolution and reprecipitation.

Decompose 2 to 10 gms. of the ore with hydrochloric and nitric acids, evaporate off the excess of acid, dilute, transfer to a stout bottle, saturate cold with hydrogen sulphide, tie the cork down, and heat for an hour in a boiling-water bath, cool, uncork, filter, and wash well. Add to the filtrate a little hydrochloric acid and potassium chlorate, and boil to oxidize sulphur and ferrous oxide.

If there be no metals of the higher groups present, of course the treatment with sulphuretted hydrogen, and after oxidation with potassium chlorate, is to be omitted. Dilute the filtrate, after boiling with hydrochloric acid and potassium chlorate if sulphuretted hydrogen has been used, or the first filtrate, after decomposing the ore with acids, if no sulphuretted hydrogen has been used, to 1 litre, and add, with constant stirring, dilute ammonia until the solution is alkaline. Then filter out the precipitated ferric hydrate, and wash slightly. Dissolve the precipitate with dilute hydrochloric acid, and precipitate again with dilute ammonia. Filter, wash, combine the filtrates, concentrated to 500 c. c., acidify slightly with acetic acid, boil, and saturate with sulphuretted hydrogen, continuing the boiling while introducing the gas. Filter out, and wash the precipitated sulphides of nickel

and cobalt, and wash them with sulphuretted hydrogen water. Should any manganese oxide be present, it will be held in solution. To recover any possible traces of nickel and cobalt, add a little more acetic acid to the filtrate, and boil. Should any sulphide be recovered by this treatment, wash it and the main precipitate from the filter into a casserole, dry and burn the filters, add the ash to the precipitates, and dissolve all with nitro-hydrochloric acid. Expel excess of acid by evaporating nearly to dryness, dilute, precipitate the oxides of nickel and cobalt by adding to the solution an excess of pure potassium hydrate, and heating for some time nearly to boiling, and separate the two metals by one of the following methods. (See Fres., *Quant. Anal.*, § 110—b— α , p. 188, and § 111.)

The first method is due partly to Liebig and partly to Wöhler. Wash the two oxides from the filter into a beaker, run through the filter, in order to dissolve what adheres, a saturated solution of pure potassium cyanide, into the beaker containing the oxides, and warm until they are dissolved. The solution looks reddish yellow. Heat to boiling to remove the free hydrocyanic acid. By this process the double cyanide of cobalt and potassium in the solution is converted, with evolution of hydrogen, into cobalticyanide of potassium, while the double cyanide of nickel and potassium in the solution remains unaltered. Add to the hot solution finely pulverized and elutriated mercuric oxide (red oxide), and boil. By this operation, the whole of the nickel is precipitated, partly as sesquioxide, partly as cyanide, the mercury combining with the liberated cyanogen. The precipitate is greenish at first, or, if the mercuric oxide has been added in excess, yellowish gray. Wash and ignite. The residue is oxide of nickel (NiO). (See Fres., *Quant. Anal.*, § 100—14—b.)

To determine the cobalt in the filtrate, Wöhler directs to carefully neutralize it with nitric acid, and add solution of mercurous nitrate, as long as it produces a precipitate of mercury cobalticyanide. The precipitate, after

washing and drying, is to be ignited with access of air, when it is weighed as black oxide of cobalt (Co_3O_4). He suggests that, on account of its oxygen varying according to the temperature, it is better to reduce it by ignition in a strong current of hydrogen, and weigh the metallic cobalt. (See Wöhler's paper in *Annal. d. Chem. u. Pharm.*, LXX., 256, or his *Mineral Analysis*, p. 102. Care must be taken in neutralizing the filtrate before adding the mercurous nitrate, as the fluid must not be acid, and must not be strongly alkaline. The ignited oxide of nickel is very apt to contain some impurities; consequently, it is better to transfer it from the crucible to a beaker, boil it with water, throw it on a filter, wash, dry, ignite, weigh again, and subtract the loss, probably some adhering alkali. Then dissolve it in aqua regia, dilute, filter, wash, dry, ignite, and weigh any undissolved silica, and deduct its weight also. Finally, add to the filtrate a large excess of ammonia, filter out, wash, dry, ignite, and weigh any alumina and ferric oxide that may be present. After deducting their weight from that of the original precipitate, the remainder will be the true weight of the oxide of nickel. From this, calculate the metallic nickel.

Another method of separating the two metals is by means of potassium nitrite, recommended by H. Rose, and Fresenius as the best. (See Fres., *Quant. Anal.* § 160-9, p. 366). Dissolve the sulphides (obtained after precipitating the basic acetates, as directed before), in aqua regia, evaporate the solution nearly to dryness, and neutralize with potassium hydrate. Then add a concentrated solution of potassium nitrite (previously neutralized with acetic acid, and filtered from any flocks of silica and alumina that may have separated) in sufficient quantity, and finally acetic acid, till any flocculent precipitate that may have formed from excess of potassa has redissolved, and the fluid is decidedly acid. Allow it to stand at least for 24 hours in a warm place; take out a portion of the supernatant fluid with a pipette, mix it with more nitrite, and

observe whether a further precipitation takes place in this after long standing. If no precipitate is formed, the whole of the cobalt has fallen down; otherwise, the small portion must be returned to the principal solution, some more nitrite added, and, after long standing, the same test applied. Finally, filter and wash the precipitate thoroughly with an aqueous solution of neutral potassium acetate (containing 10 per cent of the salt), displace finally the last portion of solution of potassium acetate adhering to the precipitate, by means of alcohol of 80 per cent, and dry. Then transfer the precipitate from the filter to a clock-glass, incinerate the filter in a weighed crucible, add the precipitate, and gently ignite all. Cool, moisten with sulphuric acid, cautiously expel excess of acid, and ignite at low red heat. Cool and weigh the sulphate of cobalt and potassium ($2\text{CoSO}_4 + 3\text{K}_2\text{SO}_4$), and calculate the cobalt. One hundred parts of the residue are equivalent to 18.015 parts CoO , or 14.17 parts Co . (See Fres., *Quant. Anal.*, § 81 or *Annal. d. Chem. u. Pharm.*, CIV., 309.)

To determine the nickel, acidify with hydrochloric acid, boil out nitrous acid, precipitate as sulphide, and convert to sulphate by treatment with sulphuric acid, using a little aqua regia if necessary. Finally transfer to a weighed platinum dish, evaporate, expel the surplus acid by gentle ignition, and weigh *yellow* anhydrous nickel sulphate. Too strong ignition will cause decomposition of the nickel salt.

Another good method of determining the nickel, and cobalt in ores, is to decompose them in the same manner as directed above, remove any metals of Groups V. and VI. with sulphuretted hydrogen in acid solution, filter, oxidize the filtrate by boiling it with hydrochloric acid and potassium chlorate; dilute to about 1 litre. If no metals of the higher groups are present, the treatment with sulphuretted hydrogen, and potassium chlorate is to be omitted, and the original acid solution diluted to about 1 litre. Then make the solution alkaline by adding dilute

ammonia, and stirring constantly. Filter out any precipitate, dissolve it with hydrochloric acid, and precipitate again in the same way. Combine the filtrates, concentrate them to 100 c. c., add a little ammonia, transfer to a weighed platinum dish, and precipitate the nickel and cobalt together in the metallic form by passing a strong galvanic current, generated from 3 or 4 Bunsen cells, keeping the solution hot (about 70° C.). Ammonia should be added from time to time, to restore what is driven off by such heating. When the separation from the solution is complete, remove the dish, wash it thoroughly with hot water, dry and weigh it. The increase in weight expresses the combined weight of metallic nickel and cobalt. It remains to separate and determine them. Dissolve them with nitric acid; separate, and determine one or both, by methods described further on.

The following method of analysis of nickel and cobalt ores is from the pen of Fresenius, published in his *Zeit. für Anal. Chem.*, and translated by Prof. C. A. Schaeffer. (See *Am. Chem.*, IV., p. 289.)

The finely-powdered mineral or metallurgical product is treated with hydrochloric acid, with addition of nitric acid, until all soluble matter has been brought into solution, and repeatedly evaporated, with addition of hydrochloric acid, almost to dryness, in order to drive off the excess of nitric acid. Dilute hydrochloric acid and water are then added to the residue, after which it is filtered. If the insoluble portion is not perfectly white it is fused with acid potassium sulphate, the mass treated with hydrochloric acid and water, filtered, and the filtrate added to the original solution. The metals of Groups V. and VI. are next precipitated by hydrosulphuric acid. For this purpose, it is well to pass the gas through the solution at first at about 70° C., and afterward in the cold. The filtered solution is then warmed, and the iron oxidized with nitric acid; ammonia in excess is then added, and the impure ferric hydrate filtered off. After washing,

this is dissolved in hydrochloric acid, the solution largely diluted, and, after addition of ammonium chloride, a dilute solution of ammonium carbonate is added, in the cold, until a point is reached where the liquid becomes cloudy, but no precipitate is visible. On standing, the liquid should not again become clear, but rather more cloudy, although the reaction at this point must be definitely acid. It is next heated to boiling, the precipitate of basic oxide of iron is washed, first by decantation and afterward on the filter with boiling water; a portion of the precipitate is then examined for nickel by dissolving it in hydrochloric acid, repeating the precipitation as basic oxide, and testing the filtrate with ammonium sulphide, in order to see whether it is perfectly free from that metal. If, in this operation, a small amount of nickel should still be found, the whole precipitate must be dissolved in hydrochloric acid, and the iron again separated as basic oxide, as above. The two, or, as the case may be, three filtrates which contain nickel and cobalt are next acidulated with acetic acid, and concentrated by evaporation. If, by this means, a trifling precipitation of ferric or aluminic hydrate take place, the precipitate must be filtered off, dissolved in hydrochloric acid, and again separated with ammonia in excess, and this operation repeated once more. The filtered solution, containing all the nickel and cobalt, having been sufficiently concentrated, is treated with sodium carbonate until the reaction is decidedly alkaline, acetic acid is then added to acid reaction, and, to the clear liquid (30-50 c. c.), a solution of sodium acetate (1 : 10) is added. Hydrosulphuric acid is then passed through the solution, warmed to about 70° C., until the latter is saturated with that gas. The separation being completed, the precipitate of the sulphides of nickel and cobalt is filtered, washed, and dried. The filtrate is concentrated by evaporation; hydrosulphuric acid, ammonium sulphide, and acetic acid are added to it, and thus frequently a little more of the sulphides of nickel and

cobalt is obtained. It is well to test the filtrate in this way once again, in order to be quite sure that the whole of the nickel and cobalt has been obtained as sulphides. The dried sulphides of nickel and cobalt, together with the filter ash, are now treated with hydrochloric acid, with addition of nitric acid, until all has been dissolved, the solution evaporated with addition of hydrochloric acid in order to drive off the nitric acid, diluted with water, filtered, and the nickel and cobalt precipitated with pure potassium hydrate in a large platinum dish. The precipitate obtained must be very thoroughly washed by decantation afterward on the filter, with boiling water, dried, incinerated and heated to bright redness in a Rose crucible, in a current of pure hydrogen, until the weight remains constant. The metallic nickel and cobalt are next treated in the crucible with boiling water. Should this show an alkaline reaction or the presence of chlorine or sulphuric acid, or yield a residue when evaporated on platinum foil, the metals must be exhausted with boiling water, heated in a current of hydrogen, and again weighed. The metals are now dissolved in hydrochloric acid, after which a small amount of silicic acid usually remains. This is to be collected on a filter, burned, and weighed. The hydrochloric acid solution is nearly neutralized with ammonia; ammonium carbonate is added in excess, and the liquid slightly warmed for some time. A trifling precipitate of ferric and aluminic hydrates, which in most cases is obtained, is filtered, dissolved in hydrochloric acid, again precipitated, and ignited, first in the air and then in a current of hydrogen. Its weight, together with that of the silicic acid, is then to be subtracted from the original weight of the metals. As can easily be seen, it will in most cases be allowable, and a great saving of time, to incinerate the little filter containing the silicic acid, and that containing the ferric and aluminic hydrates in the same small crucible, and then, after treatment with hydrogen, to weigh all these impurities together. Should,

however, the ash of these, in consequence of the presence of a small amount of cobalt, appear bluish, it must be fused with an alkaline carbonate, and the silicic acid, etc., thus obtained be perfectly pure.

If the ore or metallurgical product contain zinc, the nickel and cobalt obtained by the above method would be contaminated with that metal, since zinc cannot be entirely removed either by the precipitation of the hydrates with excess of potassium hydrate, or by the reduction of the oxides in a current of hydrogen. In this case, the hydrochloric acid solution of the metals precipitated by ammonium sulphide is evaporated to a small volume; and pure, finely-crystallized ammonium chloride is added to it in such quantity that, for 0.2 gm. oxide of zinc, there shall be about 5 gms. ammonium chloride. It is then evaporated to dryness on a water-bath, and carefully heated, until all the ammonium chloride, and with it all the zinc, is driven off. The residue, which contains the salts of nickel and cobalt, is dissolved in hydrochloric acid, with the addition of nitric acid, the greater part of the excess of free acid driven off, and the oxides precipitated with potassium hydrate, and further treated exactly according to the above method.

If nickel and cobalt are to be determined separately, the ammoniacal filtrates, obtained after separation of the contaminating substances, are evaporated to dryness, the ammonium compounds are driven off by gentle heat, the residue dissolved in hydrochloric acid, with addition of nitric acid, and if much nickel and little cobalt are present, the latter is separated by means of potassium nitrite. If, on the contrary, much cobalt and little nickel are present, it is found more advisable to add, to the solution of the chlorides, potassium cyanide in excess, and to precipitate the nickel as the black hydrate oxide of nickel, by warming with bromine after the addition of the potassium hydrate. In the first case, the potassio-cobaltic nitrite, and in the second, the hydrated oxide of nickel, is dis-

solved in hydrochloric acid, precipitated with potassium hydrate, and determined in the metallic condition. In these determinations, the weighings must be followed by an examination for silicic acid, and impurities insoluble in ammonium carbonate.

It will be noted that several different ways of separating nickel for weighing are given. The oldest method consists in the precipitation as hydrate by means of potassium hydrate. Another method not before mentioned consists in precipitating by bromine with potassium hydrate. This latter gives a black precipitate of $\text{Ni}_2(\text{OH})_6$. In either case by strong ignition *green* NiO is obtained. Either method, however, presents difficulties, first in washing all the alkali from the precipitate, and secondly in that silica, alumina, and ferric oxide are almost invariably found in the precipitate. Rose's method of obtaining the metals by reduction with hydrogen is now hardly ever used, and does not obviate these difficulties.

Determining nickel as yellow anhydrous sulphate requires careful management to avoid overheating, and consequent decomposition of the salt. The electrolytic separation is now usually preferred. For economy of time, it is necessary to conduct the operation in a hot solution (70° to 90°C.), and with a strong current (about 3 amperes). The solution must be *always* kept ammoniacal by frequent additions of ammonia. The chloride solution may be used if much ammonium chloride is present, and no fixed alkaline or alkaline-earth chlorides. An oxalate solution containing an excess of ammonium oxalate is recommended by Classen, but the solution most frequently used is that of the sulphate (containing of course ammonium sulphate, as well as free ammonia). Iron (in ferrous form), zinc, or copper will also be partially or entirely deposited under the conditions named, so that their absence must be insured to obtain accurate results.

CHAPTER XXII.

COPPER ORE.

A qualitative examination should first be made, directing the tests more particularly to the detection of zinc, nickel, lead, bismuth, arsenic, antimony, and tin.

Incidentally a rough estimate of the proportion of copper present should be made, as a guide to the amount it will be best to take for the quantitative estimation.

An amount containing approximately 0.2 gm. of copper is the most convenient.

The finely pulverized ore may be treated directly with solvents, or if it consists largely of sulphides, especially when arsenic or antimony is present, time may be saved by roasting a weighed portion in a porcelain capsule before applying the solvents. In any case, transfer the powder to a small flask, add 5 c. c. of nitric acid, and apply heat, adding hydrochloric acid from time to time, and keeping up the treatment until the material has apparently been all decomposed. Then add 6 or 8 c. c. of concentrated sulphuric acid and heat until dense fumes of sulphuric anhydride are seen *inside* of the flask.

Cool, dilute with about 50 c. c. of water, and filter from the insoluble residue. If lead is present, it will have been partially dissolved in the concentrated sulphuric acid, but precipitated by the dilution, and it will be advantageous to allow it to stand for some little time after dilution, that the lead sulphate may collect in granules of sufficient size to be the more readily filtered off. The insoluble residue should be carefully tested for copper; if any is found, it should be treated again with acids, and the solution added to the first one.

The solution now contains presumably all the copper, but may contain certain elements liable to interfere with

its correct estimation, so that it may be necessary to apply some further treatment before proceeding to its determination. Arsenic, antimony, bismuth, and tin may interfere with the electrolytic determination. Zinc and nickel affect seriously the accuracy of the cyanide titration, while arsenic, antimony, lead, iron, and nitrous acid (or lower nitrogen oxides) prevent accurate results in the iodide method.

In many cases interfering elements may not be present for the method intended to be used, and the introduction of any extra step at this point may be avoided.

The copper may be separated from the members of the ammonium-sulphide group by precipitation with hydrogen sulphide. This process, however, does not separate it from the other elements mentioned (arsenic, etc.), and if those were not separated by a preliminary roasting of the ore, the sulphides obtained at this point should be subjected to roasting in a porcelain capsule, when the residual copper oxide may be brought into solution in nitric acid, and converted into sulphate, or treated in the form of nitrate by whatever process may be selected.

Another method for separating the copper consists in adding to the solution (of sulphate) a few small granules of zinc, and precipitating in the metallic form. The best way of managing consists in adding so small an amount of zinc that the excess may be completely dissolved in the free acid of the solution. One must, however, be certain to add enough zinc to precipitate all the copper. Magnesium or metallic iron may be used instead of the zinc. The spongy copper may then be filtered off, washed, and dissolved in nitric acid, etc., as before. This method cannot, however, be relied upon to separate the copper entirely from arsenic, antimony, tin, or bismuth. The last two are not of very frequent occurrence in copper ores.

Electrolytic Separation.—An acid solution is usually used. Not over 8 per cent of free acid should be present in the solution. Some use a solution containing only sul-

phates and some free sulphuric acid. Under these conditions the presence of even small amounts of arsenic or antimony affords a dark-colored deposit more or less contaminated with those elements. The addition of a few drops of nitric acid gives a bright coating, and prevents to a very considerable extent such contamination. It does not, however, entirely prevent the deposition of bismuth, except under special conditions. Some use a solution consisting entirely of nitrate with free nitric acid, and this plan is the most general. The presence of lower oxides of nitrogen prevents the deposition to a very marked extent. Whenever nitric acid or nitrates are present in the solution, the current must not be interrupted at the close of the operation until the dish has been "flooded out," *i. e.*, the solution drawn off while water is poured in, until the acid has been so much diluted, or washed out, that it exerts practically no solvent action on the copper, when the circuit is broken. Also, when nitric acid is present, zinc, and possibly nickel, if in the solution, will begin to deposit to a slight extent, as soon as all of the copper has been separated out.

Hydrochloric acid and chlorides are not permissible in a solution for quantitative electrolysis. The presence of organic acids (citric, tartaric, etc.) is also inadmissible. The deposit from solutions containing those acids is bright, and apparently pure, but the copper is brittle, and contains organic elements. (Mackintosh, *Am. Chem. Jour.*, III., 354.)

As to the source of electricity, for a single deposition, a one-gallon gravity cell when in good working order will usually suffice. For more depositions at the same time two or three gravity cells will be more satisfactory. If the connection is made with an electric-light current some form of resistance must be interposed. A good plan consists in passing the current through acidulated water in a jar before allowing it to pass through the solutions. By arranging the poles in this jar so that they can be

brought near to one another or separated according to requirements, any degree of resistance necessary for the purpose may be obtained. An incandescent lamp in a circuit of suitable strength for the deposition of copper should only show a glow just perceptible in full daylight—not in direct sunlight. Too strong a current will give a dull spongy deposit, not always perfectly adherent. A platinum evaporating dish, containing the liquid analyzed, is frequently used as the kathode, the anode being a strip of platinum foil hung in the solution. A much less expensive arrangement consists in using a glass beaker as the containing vessel, and having for the electrodes cylinders made of platinum foil. The connections should be so made that with a number of depositions the entire current should pass through the solutions successively. If, as is sometimes the case, the connections are so made that the current can pass partially or entirely through any one of the solutions, irregular and unsatisfactory results are inevitable.

To determine when all of the copper has been precipitated, tilt the dish or the electrode so that the liquid covers a fresh surface of the platinum, and note whether any further precipitation is perceptible. This may not serve the purpose always, because it may happen that the solution has become too acid by loss of copper. It is therefore well at the same time to add a little water, to dilute the free acid which may be present. Other tests may be applied, as hydrogen sulphide in a few drops taken in a watch-glass (serviceable only in the absence of other metals giving dark-colored sulphides in acid solutions) or potassium ferrocyanide (not applicable if iron is present).

Some analysts draw off the solution after most of the copper has been deposited (say after two hours), add ammonia, dilute to a convenient bulk, and then, with the aid of an ammoniacal solution of copper of known strength, estimate colorimetrically the amount of copper still in

solution. The copper solution for comparison may contain 0.001 gm. of metal per c. c.

A dark color to the precipitated copper does not necessarily mean the presence of a weighable amount of impurity, but is best avoided.

After washing with water rinse off the water with alcohol, and dry off the adhering alcohol by holding the dish or electrode in the hand over a burner, removing it at intervals, and in this way making sure that the coating is not exposed to a heat higher than can be borne by the hand. Cool and weigh.

The electrolytic determination of copper is so generally used in this country that it has been called the "United States method."

Determination as Oxide.—After obtaining a solution of copper, free from other substances precipitable by fixed alkalies, the solution is brought to boiling, and caustic soda or potassa solution is added until it is decidedly alkaline. In the absence of organic matter copper is completely precipitated as black oxide. (If a boiling heat is not maintained, blue copper hydrate may be temporarily formed.) Wash thoroughly by decantation, and then on the filter until the washings show no alkalinity. Dry, ignite, and weigh CuO . Results are frequently high, on account of the difficulty in washing out the alkali. The ignited precipitate also is hygroscopic. If the filter-paper is destroyed by the aid of nitric acid there is some danger of mechanical loss on igniting.

VOLUMETRIC METHODS.

The cyanide method is much used in spite of many inherent defects. The method depends upon the fact that the addition of potassium cyanide to an ammoniacal copper solution affords a colorless solution containing cuprous ammonium cyanide and other compounds.

The results are influenced by the proportions of copper,

of free ammonia, and of ammonium salts present, by the bulk of the solution, and by the presence of many of the metals other than copper. Zinc and nickel salts produce the most marked effect. Hence, for accurate work, the absence of zinc, nickel, etc., should be insured, and the same bulk of liquid, containing approximately the same relative proportions of copper, of ammonia salts, and of free ammonia, should be used in standardizing, and for each test.

Convenient proportions are: Copper salt containing about 0.2 gm. metallic copper, as nearly as can be judged from a qualitative test on the ore.

The (nitric or sulphuric) acid solution should be evaporated to about 3 c. c., and after dilution to 300 c. c., 10 c. c. of strong ammonia should be added.

It may be found convenient to adopt other proportions, but uniformity in these details in standardizing and testing are indispensable.

The strength of potassium cyanide solution for most work is 55 gms. KCy per litre. Of this 1 c. c. is equivalent to about 0.01 gm. Cu. A solution of half this strength or even less is preferred by some.

To standardize, dissolve 0.2 gm. of pure metallic copper in dilute nitric acid, evaporate to 3 c. c. to remove nitrogen oxides and excess of free acid, dilute to 300 c. c., and add 10 c. c. of strong ammonia. Then run in the cyanide solution from a burette, stirring it well in. The addition may be moderately rapid at first, but must be slow toward the end. When the titration is nearly finished, the solution assumes a pinkish ("peach-blossom") tint. At that point the cyanide solution is to be added not faster than two drops at a time, and after stirring, the mixture must stand for a full minute or more before the next addition. When complete decolorization has been effected, read the burette, and calculate the value of 1 c. c.

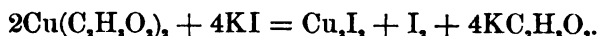
For the analysis of an ore or metallurgical product an amount must be taken which will yield approximately

0.2 gm. of copper (or the amount used in standardizing), which is treated in the manner already described, so as to obtain a solution of the copper free from zinc or nickel (most conveniently a nitric acid solution), evaporate to 3 c. c., dilute to 300 c. c., etc., proceeding as when standardizing.

If the solution of copper contains ferric iron, the addition of ammonia precipitates ferric hydrate, which will persistently retain some copper, even after careful washing, so that tests on the clear liquid after filtering would be inaccurate. The titration can be conducted with the ferric hydrate suspended in the solution, but it then becomes a matter of extreme difficulty to note the exact point of decolorization.

It has been noted that copper is not precipitated by solutions of fixed alkaline bicarbonates, and it is reported that in copper solutions containing sufficient free acid to convert the sodium or potassium carbonate which may be added into bicarbonates clear solutions may be obtained, in which more satisfactory results are afforded by the cyanide titration than in ammonia solutions. (*Vid. Ch. News*, LVIII., 131, and LXI., 183.)

The iodide method depends upon the reaction :



Cuprous iodide precipitates, and a proportionate amount of iodine is set free, which may be determined by titration with sodium thiosulphate. Salts of iron, lead, bismuth, arsenic, antimony, and perhaps some others, influence the reaction, so that a solution of the copper must be obtained free from those elements by methods already described. Nitrous acid and lower nitrogen oxides also interfere, and must be removed by evaporation. Free mineral acids tend to decompose the potassium iodide, so that no free acid stronger than acetic should be present. This condition is readily attained by adding to the solution a slight excess of sodium carbonate, and then acidifying with acetic acid.

The only standard solution required is that of the sodium thiosulphate. The crystallized salt is $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$; but it is practically impossible to obtain it for laboratory purposes containing no more or no less than the exact amount of water of crystallization. 39.3 gms. of the theoretical salt per litre would afford a solution of which 1 c. c. would be equivalent to 0.01 gm. Cu. It is usually preferable to make a solution of about half this strength.

One requires also a ten per cent solution of potassium iodide, also a starch solution; the latter is best made by crushing up about 1 gm. of starch in a mortar, adding 10 drops of strong solution of caustic potash or soda, grinding to a paste with a little lukewarm water, and diluting with warm water to about 500 c. c. Thus prepared, it will keep indefinitely. If made without alkali it soon moulds and spoils.

To standardize the thiosulphate solution proceed as follows:

Prepare a solution of 0.100 or 0.200 gm. of pure metallic copper in the same manner as for the cyanide titration. After evaporating off lower nitrogen oxides and most of the excess of free acid, rinse into a flask of about 200 c. c. capacity with 80 to 100 c. c. of water. Add sodium carbonate until a permanent precipitate is obtained, and then acetic acid until all is dissolved. Then add 10 c. c., or an excess, of the potassium iodide solution. The mixture at once shows the deep yellowish-red color due to dissolved iodine, the precipitate of cuprous iodide forming at the same time. Now run in the thiosulphate solution from a burette until the solution has only a faint yellow color. The cuprous iodide being nearly white, does not prevent this from being readily seen. Now add a few drops of the starch solution, and continue the addition of the thiosulphate until the blue color of the starch iodide is just destroyed. As the end of the operation approaches, it is well to remember that the cuprous iodide in itself possesses a faint pinkish tinge, or the stopping point may not

be accurately noted. The starch solution should *never* be added until most of the free iodine has been removed, or the iodine will react upon the starch in such a way as to produce erroneous results. The reaction for the titration is: $2\text{Na}_2\text{S}_2\text{O}_3 + 2\text{I} = 2\text{NaI} + \text{Na}_2\text{S}_4\text{O}_6$.

The solution from an ore, etc., is tested in essentially the same manner.

Colorimetric Methods.—The colorimetric method with ammonia has already been suggested.

Another method for small amounts of copper (T. Carnelly, *Ch. News*, XXXII., 308) depends upon the coloration produced by adding potassium ferrocyanide to the *neutral* solution. The delicacy of the reaction is heightened by the addition of ammonium nitrate to the solution.

CHAPTER XXIII.

NICKEL ALLOYS, GERMAN SILVER, ETC.

The metals to be looked for usually are copper, nickel, zinc, and iron, which last is sometimes added to make the metal white. Lead is sometimes found in small quantity.

Introduce 0.500 gm. of the alloy into a 200 c. c. flask, add 5 c. c. of concentrated nitric acid, and 15 c. c. of water, and heat until the alloy is dissolved. Then cool, add 10 c. c. of concentrated sulphuric acid, and heat until dense fumes of SO_3 are evolved. Cool, dilute to 50 c. c., and filter out lead sulphate, if necessary. Divide the filtrate into 2 equal parts, and determine the copper in each electrolytically, as directed in the analysis of copper ore. Combine the solutions (after precipitating the copper) together with the washings (after boiling out the alcohol from them), add sodium carbonate until the fluid is slightly alkaline, and then acetic acid until it is acid, and precipitate basic ferric acetate as usual. Dissolve the precipitate in hydrochloric acid, re-precipitate the ferric hydrate by ammoniac hydrate, filter, dry, ignite, and weigh, and calculate it to metallic iron.

To the filtrate, add pure potassium hydrate in large excess. Nearly all the zinc will be held in solution, while the nickel, with, perhaps, a little zinc, will be precipitated. Allow the precipitate to settle, decant the clear fluid into another vessel, and add to the precipitate a few c. c. of a clear, concentrated solution of potassium cyanide. Warm gently to dissolve the nickel hydrate. If necessary, add more of the cyanide; avoid any large excess. If a yellow turbidity of iron hydrate remains, filter it out, and, as it contains no zinc, dissolve it in hydrochloric acid and potassium chlorate, and reserve it to be added to the solu-

tion containing the nickel after precipitating the zinc. Combine the other solutions containing zinc and nickel, neutralize with hydrochloric acid, leaving the fluid only slightly alkaline, add potassium sulphide until all the zinc is precipitated, filter, and determine the zinc as directed in analysis of zinc ore.

Add to the filtrate from the zinc sulphide, the solution of the small portion which resisted the action of potassium cyanide, add more hydrochloric acid, if necessary, and boil, to decompose the cyanides, and expel cyanogen. Then make the solution strongly alkaline with ammonia, filter out any ferric hydrate, calculate it to metallic iron, and add the per cent to that obtained from the acetate. In the ammoniacal filtrate from the ferric hydrate, determine the nickel electrolytically, as in the analysis of nickel ore.

As the above operations may introduce such amounts of salts as to interfere with concentration for the battery precipitation, it may be preferable to precipitate out the nickel and redissolve. In such a case add ammonium sulphide—stir it in well—render just acid with acetic acid, and allow the solution to stand for some time. Then decant through a filter, allowing as little of the precipitate as possible to get upon the filter; dissolve the precipitate in hot nitric acid, destroy the carbon of the filter by fusing with a small amount of alkaline nitrate, and add to the solution of the precipitate. The neutralization by ammonia, etc., may then be conducted as usual.

NOTE.—In the analysis of these alloys, the separation of zinc from nickel is the most important point. The cyanide method described is most favored. *Moore* (Chem. News, LII., 20) describes a modification, consisting in evaporating the filtrate from copper to dryness—adding potassium cyanide in amount sufficient to dissolve the precipitates of zinc and nickel which form at first, adding ammonium sulphide, diluting and boiling until the steam has no action on test papers. Zinc is separated as sulphide, together with any iron that may be present, the nickel remaining dissolved. After filtration, the nickel cyanide is destroyed by acidifying with hydrochloric acid and digesting with bromine water, and the nickel may be separated by precipita-

tion as hydrate, or by electrolysis. The zinc and iron may be separated by repeated re-solution and reprecipitation with ammonia.

Zimmermann's modification (*Liebig's Annalen*, CXC., 1) consists in adding sodium carbonate to the (acid) solution of these metals until a slight permanent turbidity is produced, then introducing an excess of ammonium sulphocyanate, saturating with hydrogen sulphide, and allowing to stand warm for some time, when zinc sulphide separates completely.

Another set of methods depend upon the relative insolubility of zinc sulphide in solutions of organic acids. These processes usually require more time for their accomplishment. The larger the excess of free organic acid, the slower the separation of the zinc sulphide.

For the *acetic acid* separation, *Baubigny* (*C. Rend.*, CVIII., 286) prescribes dilution until the solution contains but 0.3 gm. of the combined nickel and zinc salts per 100 c. c., adding ten per cent of glacial acetic acid, saturating at ordinary temperature with hydrogen sulphide, and allowing to stand for three hours. Heating and passing the gas will bring down nickel sulphide as well.

In the *formic acid* method (*Hampe*, *Chem. Ztg.*, IX., 543; also *Bragard*, *Fres. Zts. Anal. Chem.*, XXVII., 209) the solution should contain about 5 c. c. of formic acid for every 0.08 gramme of nickel, the solution being diluted to 500 to 600 c. c. Precipitation by hydrogen sulphide in the cold is to be preferred, or the proportion of acid should be increased.

In the *citric acid* method (*Beilstein*, *Berichte*, XI., 1715) the solution must be completely neutralized, then acidified with citric acid, saturated cold with hydrogen sulphide, and allowed to stand for 24 hours.

The *oxalic acid* method (*Carnot*, *C. Rend.*, CII., 678) is managed in essentially the same manner, using oxalic acid instead of citric.

In the *succinic acid* method (*Alt and Schultze*, *Berichte*, XXII., 3259) only succinates should be present. The metals are precipitated out by sodium carbonate, and the precipitate dissolved in succinic acid. Then, on passing hydrogen sulphide, zinc only is precipitated as sulphide, as in the case of the others.

CHAPTER XXIV.

GALENA AND LEAD ORES.

Introduce into a flask holding about 200 c. c., 1 gm. of finely pulverized galena, previously dried at 100° C., add 4 or 5 c. c. of red fuming nitric acid, and cover with a watch-glass. After the violent action is over, heat on a water-bath for some time, to oxidize the sulphur. After the sulphur is oxidized, add 3 or 4 c. c. of sulphuric acid previously diluted with 3 or 4 c. c. of water, and heat over a burner until the nitric acid is expelled, and dense white fumes of SO₂ appear. Then cool, dilute cautiously with about 50 c. c. of water, filter, and wash the residue, containing lead sulphate and gangue, with about 100 c. c. of water containing 1 per cent of sulphuric acid.

Difficulty is sometimes experienced in completely decomposing galena by nitric acid alone. This is chiefly due to the formation of lead nitrate insoluble in the strong acid used, which protects the undecomposed portion. The remedy is to add a little concentrated hydrochloric acid, which forms lead chloride, soluble in the strong acids present. In the subsequent separation, however, the presence of nitrates or chlorides is undesirable, so that heating with excess of sulphuric acid until only strong sulphuric fumes escape, is important. Lead sulphate is soluble in concentrated sulphuric acid, but in the dilute acid it is less soluble than in pure water. On dilution, therefore, we obtain an insoluble residue of gangue mingled with all of the lead as sulphate.

From this residue the lead sulphate may be separated after filtering and washing with dilute sulphuric acid, most of the bases in the ore, other than lead, going into the filtrate. The means employed to separate the lead may be: treating with ammonium chloride, acetate, citrate,

or tartrate; or boiling with alkaline bicarbonate, filtering and washing off the sodium sulphate formed, and then dissolving the lead carbonate in acetic (or nitric) acid.

Ammonium chloride or acetate dissolves lead sulphate best when a strong and hot solution of the neutral salt is used; citrate and tartrate have the strongest solvent effect, when they contain an excess of ammonia. Such solutions, however, rapidly absorb carbonic acid from the air of the laboratory, causing a reprecipitation of much of the lead.

The variety of methods which have been, or may be, used might be thus summarized:

Solvent for PbSO_4	Separate by	Weigh as
NH_4Cl	Metallic Al or H_2S	Metallic Pb or PbSO_4
$\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$	$\text{K}_2\text{Cr}_2\text{O}_7$ or H_2S	PbCrO_4 or PbSO_4
$(\text{NH}_4)_2\text{C}_2\text{H}_3\text{O}_6$	H_2S	PbSO_4
$(\text{NH}_4)_2\text{C}_2\text{H}_3\text{O}_6$	H_2S	PbSO_4

The hydrogen sulphide separation should be effected in an acidified solution; after washing, the precipitate is treated in the same manner as the original ore, *i. e.*, decomposed by use of nitric acid, with or without the aid of hydrochloric, and then converted to sulphate by evaporation with excess of sulphuric acid. The final evaporation should be performed in a weighed porcelain capsule. By this means one can avoid the difficulties and dangers incident to filtering through paper, and incinerating the paper in contact with more or less lead sulphate. The heat is continued until all free sulphuric acid has been expelled, leaving lead sulphate to be cooled and weighed.

The separation of the lead as chromate cannot be completely effected in solutions containing ammonium citrate or tartrate, nor indeed in warm solutions containing much ammonium acetate. After washing and drying, the precipitate cannot be ignited without loss, but must be weighed on a weighed filter. Ferric compounds, if present in the solution, will cause high results by contaminating the precipitate.

Precipitation of the metal from the ammonium chloride solution of the sulphate by metallic aluminum is a method advocated by von Schultz and Low.

The method is essentially as follows: the mixture of lead sulphate and gangue is treated with a boiling solution of ammonium chloride saturated in the cold. The solution is run into a flask, containing two or three strips of aluminum foil ($\frac{1}{2}$ by $1\frac{1}{2}$ inches). When precipitation is complete, the flask is inverted over a (weighed) porcelain capsule so that the aluminum foil and spongy lead fall into it. The lead adhering to the foil is rubbed off *under water*, and the foils are withdrawn. Then by means of an agate pestle the lead is pressed into a coherent sheet, which is washed first with water, finally with alcohol, and then dried and weighed. The aluminum foil must be quite pure or the results will be high.

For obtaining a solution of the lead, when the sulphate is mixed with the gangue, the alkaline bicarbonate separation is the best, since by that means one may get a solution free from such alkaline salts as may interfere with subsequent operations. It is necessary that the alkaline solution used should contain more carbonic acid than will suffice to form neutral carbonate, to prevent lead from dissolving in the first stage. Rinse the lead sulphate and gangue from the filter into a flask with about 80 c. c. of cold water, add about 2 gms. of sodium hydrocarbonate, and boil vigorously for 20 to 30 minutes. Wash (by decantation so far as may be) until the washings give no cloud with barium chloride. Then dissolve out the lead (now as carbonate), with as little acetic acid as possible.

It is advisable to treat the insoluble residue a second time with the alkaline solution, etc., to insure the extraction of all the lead. If the original ore contained much calcium, some of that element, possibly others, may go into the acid solution with the lead. From this solution the lead may be separated directly as sulphate; or as sulphide which is afterward converted into sulphate for

weighing; or as chromate either for weighing, or for estimation by the volumetric process given below.

In some commercial analyses of ores, close determinations of the lead are not required. Lead smelters usually regard the ordinary fire assay as sufficiently close for their purposes. This is estimated as giving results 3 per cent or more below what is found by wet analysis.

For volumetric estimation of lead, precipitation by standard solution of potassium dichromate may be used. The lead solution should contain practically no free mineral acid, or the end-reaction will not occur promptly. Any large excess of free acetic acid should be removed by boiling. The end-reaction is when a drop of the solution after stirring shows a red tinge with a drop of *dilute* silver nitrate solution on a porcelain plate indicating an excess of chromate. Also, as a rough guide, the precipitate settle out quickly as soon as a slight excess of chromate has been added. 14.223 gms. of potassium dichromate dissolved in one litre of water afford a solution of which 1 c. c. = 0.01 gm. Pb. Modifications of this process have been proposed, such as adding an excess of standard dichromate and titrating the excess with standard ferrous ammonium sulphate, etc.

CHAPTER XXIII.

TIN ORE.

There are many methods proposed for the determination of tin in ores. Probably, the fusion of the ore with sulphur and sodium carbonate is, as Rose remarks, p. 392, the best. It requires, however, the exercise of great care and judgment to make it successful. It is as follows:

Fuse 1 gm. of rich ore, very finely pulverized, with 3 parts of sulphur, and 3 parts of dry sodium carbonate (after mixing the ore and flux thoroughly), in a large porcelain crucible, for about one hour, over a Bunsen burner. 8 to 10 gms. of sodium hyposulphite may be used instead of the sulphur and sodium carbonate. Cover the crucible, and do not heat too highly. Fully one hour of fusion is necessary. By the fusion, sulphides of tin and sodium are produced, and, upon adding water, the tin sulphide should go into solution in the sodium sulphide, as sodium sulpho-stannate, and will—if the fusion has been properly conducted. After fusing as directed, cool, place the crucible in a casserole, add hot water, and digest on a water-bath until the fused mass is disintegrated and removed from the crucible. Then filter, wash thoroughly with hot water, and acidulate with sulphuric acid, to precipitate the tin sulphide. Allow the sulphide to settle completely, in a warm place, pour the clear fluid on a filter, wash 4 or 5 times by decantation, and then moderately on the filter with hot water. Should the precipitate show an inclination to run through the filter, wash with solution of ammonium acetate (Bunsen). Put the filter, with the not yet quite dry precipitate on it, into a weighed porcelain crucible, and apply a very gentle heat, with free access of air, until the odor of sulphurous acid is no longer perceptible. Increase the heat now gradually, to

a high degree of intensity, and treat the residue repeatedly with some carbonate of ammonia, in order to insure the complete expulsion of the sulphuric acid which may be present. Were you to apply a very intense heat from the beginning, fumes of stannic sulphide would escape, which burn to binocide (H. Rose, p. 393). The residue left after the first fusion and solution, should be fused again, and treated in the same way; and even a third and fourth time, or until no more tin can be recovered.

After weighing the stannic oxide, it should be examined for silica. To do this, weigh out a portion, and fuse it with 3 or 4 parts of a mixture of equal weights of sodium and potassium carbonates, boil with water, filter, wash, acidulate the filtrate with hydrochloric acid, and should silica separate, filter, and reserve the filter and contents. Then precipitate the tin with sulphuretted hydrogen, filter out the sulphide, and treat the filtrate as usual for silica, finally filtering through the reserved filter, already containing some silica. Calculate the silica thus found, to the whole amount of stannic oxide, and, after deducting it, calculate the metallic tin.

Examine the residue left (after fusing, and filtering out the solution of alkaline stannate as directed above) for iron, by dissolving it in hydrochloric acid and a few drops of nitric acid, and precipitating the ferric hydrate with excess of ammonia. Should any be found, it must be calculated to the whole amount of stannic oxide first weighed, and deducted from it, as was the silica. It must be calculated also to metallic iron, and the per cent added to that found elsewhere.

NOTE.—In most technical laboratories, the fire assay with potassium cyanide is applied to tin ores. (*Mitchell*, Manual of Assaying; *Ricketts*, Notes on Assaying, etc.; also, *Hoffmann*, Am. Inst. Min. Eng., XVIII., 3; *Rennie* and *Derrick*, J. S. C. I., XI., 662; *Peele*, S. of M. Quarterly, XIV., 216; etc. For comparison of methods, vid. *Miller*, S. of M. Quarterly, XIII., 368.) Analysts generally agree that it is best to concentrate from a weighed portion of the ore (cassiterite) by boiling with aqua regia, and careful vaning, which can be accomplished without loss of tin, if carefully done. Roasting is also recommended by some. Such concentration may also be advantageous preliminary to a wet analysis.

CHAPTER XXVI.

TIN ALLOYS, BRONZE, ETC.

The principal metals to be looked for are copper, tin, lead, zinc, and iron.

Dissolve 1 gm. of the alloy, in a small covered beaker, in a mixture of 2 c. c. of nitric acid, 8 c. c. of hydrochloric acid, and 10 c. c. of water, dilute to 500 c. c.; heat gently, add crystals of sodium carbonate until a distinct precipitate forms, and boil 10 or 15 minutes; the precipitate then turns black. Then cool, add nitric acid, drop by drop, until the reaction is distinctly acid, and digest for several hours at a gentle heat until the stannic oxide is white. Then filter it out, wash, dry, ignite strongly, and weigh it. The stannic oxide must then be examined for silica and iron (as directed in the analysis of tin ore), which are to be deducted before calculating the tin. This is known as Brunner's method.

The ignited stannic oxide may be purified, by first treating it with sulphuric acid and ammonium fluoride (the silica being determined by loss), and then fusing it with the two carbonates, as in analysis of tin ore, dissolving and filtering out the stannate, and in the residue determining the ferric oxide, to be deducted from the stannic oxide, and also calculated to metallic iron, the per cent of which is to be added to that found elsewhere.

Evaporate the filtrate from the stannic oxide, after adding about 10 c. c. of sulphuric acid, until fumes of SO_2 are evolved, dilute, filter out lead sulphate, and calculate lead. (See analysis of galena.)

After filtering out the lead sulphate, and washing, determine the copper in the filtrate electrolytically. (See analysis of copper ore.)

In the residual fluid, after extracting the copper, precip-

itate the zinc by sodium carbonate, and proceed as directed in the analysis of zinc ore. Dissolve the weighed zinc oxide in hydrochloric acid, filter out and determine any residual silica, and deduct its weight from that of the oxide. Then add to the filtrate, excess of pure potassium hydrate; filter out and wash the ferric hydrate, dissolve it in hydrochloric acid, and precipitate again with potassium hydrate, filter, wash, dry, ignite, and weigh the ferric oxide, which is also to be deducted from the first weight of zinc oxide. The remainder, after deducting the weight of silica, and that of ferric oxide, is to be calculated to zinc.

Combine the weight of ferric oxide found here, with that found in the purification of the stannic oxide, and calculate to metallic iron.

In all cases where there may be any suspicion of a lack of homogeneity in the alloy, 5 gms. (or more) of clippings from different parts of the sample should be taken for analysis, and aliquot parts of the solution obtained are then to be examined.

In many laboratories the method of analysis preferred consists in dissolving by the use of nitric acid alone. Acid of a specific gravity 1.2 (or weaker) should be used. Stronger acid attacks the alloys containing tin, too slowly to be satisfactory. The plan then would be:

Dissolve in dilute HNO_3 (1:1½ or 2), evaporate low, dilute with boiling water, boil, let settle, decant off, digest with dilute HNO_3 (1:6), and filter.

<i>Ppt. A.</i> H_2SnO_3 ($\pm \text{As}_2\text{O}_3$, P_2O_5 , CuO , Fe_2O_3). Digest wet with K_2S solution; filter.	<i>Sol'n A.</i> Pb , Cu , Zn , Fe , etc., as nitrates. Evaporate with H_2SO_4 to fumes, dilute, filter.
<i>Res.</i> CuS + FeS ; incinerate, dissolve in HNO_3 ; add to sol'n A.	<i>Sol'n.</i> K_2SnS_3 \pm K_2AsS_4 , K_3PO_4 , etc.* Acidify with H_2SO_4 .
<i>Ppt.</i> SnS_2 . Wash with dilute NH_4Cl . Roast to SnO_2 , ignite strongly, add a little solid $(\text{NH}_4)_2\text{CO}_3$, ignite to constant weight; calculate SnO_2 to Sn .	<i>Solution.</i> K_2SO_4 , K_3PO_4 , etc. Reject.
	<i>Precipitate</i> PbSO_4 . Determine PbSO_4 . Vid. Galena.
	<i>Sol'n.</i> Pass H_2S . <i>Ppt.</i> CuS . <i>Sol'n.</i> Fe and Zn . Dissolve in HNO_3 . Vid. Determine Cu ore. Vid. Cu ore.

* If As is present, add MgCl_2 (a little NH_4Cl) and NH_4OH , let stand cold, filter off $\text{MgNH}_4\text{AsO}_4 \pm \text{MgNH}_4\text{PO}_4$. Treat filtrate as above, acidifying with H_2SO_4 , etc.

In omitting the use of hydrochloric acid, one avoids any danger of loss of stannic chloride on evaporating, a phenomenon which may occur at a certain degree of concentration. Such loss may be prevented by addition of potassium (or sodium) chloride to the solution in sufficient quantity to form double chlorides (2KCl , SnCl_2 , etc.) from which the tin is not volatilized during evaporation.

When diluted nitric acid alone is used as the solvent, the solution should be concentrated (after all the metal has been attacked) nearly to dryness, to effect the separation of the tin in the form of metastannic acid, as well as to drive out excess of nitric acid and the nitrogen oxides; the solution must then be diluted with boiling water, and, after boiling a short time, allowed to stand and settle. The clear supernatant solution is then decanted off through a filter, and dilute nitric acid (1 to 6 by volume) poured over the precipitate, which is then digested warm for an hour or two. The separated metastannic acid ($\text{H}_2\text{Sn}_2\text{O}_7$) which should be perfectly white, may then be filtered off and washed.

This mode of procedure is open to the objection that some copper oxide (and possibly some ferric oxide) may remain with the metastannic acid. For some purposes, the results may be regarded as sufficiently close, to reckon the weight of this precipitate (after strong ignition as SnO_2), provided it appears to be but little colored after ignition.

For accurate results, however, the hydrated metastannic acid, without drying, should be digested warm (paper and all) with two successive lots of potassium sulphide solution, which dissolves the tin as sulphostannate, leaving copper and iron sulphides behind. The filtered solution of sulphostannate is then acidified with sulphuric acid, precipitating stannic sulphide, which, after filtering, etc., is carefully roasted to stannic oxide, ignited strongly, and weighed. After weighing, it is well to add a few small pieces of solid ammonium carbonate, and ignite and weigh

again, to make sure that all sulphuric acid and combined water have been removed. Any tendency on the part of the stannic sulphide to run through the filter during washing, may be checked by the addition of an acidified solution of an alkaline acetate (preferably that of ammonium).

If the alloy contained arsenic, that element would have precipitated with the metastannic acid as arsenate (2SnO_2 , As_2O_5) and the above treatment would not separate it, since the stannic arsenate is not decomposed on ignition. In that case it would be necessary to precipitate ammonio-magnesium arsenate from the sulphostannate solution (by adding magnesium chloride and ammonia) before acidifying to precipitate stannic sulphide.

The small amount of copper and iron sulphides which adhere to the filter papers on filtering off the sulphostannate solution, can be recovered by moistening the papers with nitric acid, incinerating, and then dissolving in nitric acid with the aid of a little hydrochloric acid if necessary. The solution must be added to the filtrate from the metastannic acid.

In that solution, lead, if present, may be separated by adding sulphuric acid and evaporating down to fumes of anhydride, diluting largely, and filtering.

In the filtrate from the lead sulphate, separate copper by hydrogen sulphide, redissolve in nitric acid, and in an aliquot portion of this solution determine copper (see copper ore).

In the filtrate from the copper, determine zinc and iron (see zinc ore, also iron ammonium sulphate).

To determine arsenic, when present in small amounts, a separate portion of from 5 to 100 gms. (or even more, according to requirements) should be taken, and the distillation method (see arsenic ore) is applied. Dissolving in hydrochloric acid and potassium chlorate—evaporating—adding ferrous salt, and distilling in a current of hydrochloric acid vapors, thus obtaining arsenious chloride.

The contents of the distilling flask should not be allowed to become too concentrated or some stannic chloride will also distil over.

In bronzes containing phosphorus, treatment with nitric acid affords phosphoric acid, which, like arsenic, accompanies the metastannic acid. The sulphostannate method described (with addition of magnesium salt) will, however, free the tin from that contaminant. To determine the phosphorus, however, it is best to take a separate portion (2 to 10 gms.), dissolve in hydrochloric and nitric acids as described in the first part of this chapter, and after dilution, to precipitate out tin, copper, arsenic, etc., by hydrogen sulphide, and in the filtrate proceed according to methods described under iron ore.

A special method for the separation of copper in alloys of this class may here be mentioned. A hydrochloric acid solution of the alloy is first made. The solution is then diluted, and saturated with sulphur dioxide. Then on adding potassium (or ammonium) sulphocyanate, copper is precipitated as white cuprous sulphocyanate, $\text{Cu}_2(\text{CNS})_2$. A solution of mixture of equal weights of ammonium sulphocyanate and bisulphite may be used as the precipitant, and the manipulation of the sulphur dioxide dispensed with. The precipitate may be dried and weighed, or dissolved in strong nitric acid and the copper determined by other methods.

CHAPTER XXVII.

ARSENIC ORE, ETC.

The determination of arsenic is more frequently required in ores or metallurgical products intended for other purposes, than in those in which arsenic is the desirable constituent.

When obtaining a solution in acids, some oxidizing agent should be used, to prevent loss of arsenic in the escaping gases. Under some conditions (presence of metal, etc.) it may be lost as arsenic (AsH_3) under others as the terchloride (AsCl_3).

Of methods for the separation and determination of arsenic, the following may be used :

Pearce's Method (Ch. News, XLVIII., 85).—Fusion with alkaline carbonate and nitrate to form the arsenate which is afterward precipitated as silver arsenate. In this compound the arsenic is determined indirectly by estimation of the silver. This method is now preferred in our metallurgical laboratories for the examination of ores.

Distillation Method (originally proposed by E. Fischer, Berichte, XIII., 1778).—This consists in distilling over the arsenic as terchloride (along with hydrochloric acid). In the distillate the arsenic is usually separated as tersulphide. This method is especially advantageous in the examination of crude metals (pig copper, etc.) when considerable amounts of material must be taken to obtain sufficient quantities of arsenic.

Separation as the pentasulphide (drying and weighing as As_2S_5) by heating a solution of arsenic acid in a closed flask after saturation with hydrogen sulphide (McCay, *Am. Chem. Jour.*, IX., 174) may prove convenient in some plans of analysis. The conditions necessary are: Presence

of all of the arsenic in the pentad form; acid solution; dilution to at least 200 c. c. for every 0.3 gm. of arsenic present; saturation *in the cold* with hydrogen sulphide; stoppering tightly (the stopper tied down); and heating for an hour in a boiling-water bath.

The details of Pearce's method are as follows: Mix 0.5 gm. or less of the well pulverized ore, with 6 to 10 times its weight of a mixture of equal parts of sodium carbonate and potassium nitrate in a large porcelain (or platinum) no crucible. Heat gradually up to fusion. If the proportion of arsenic is large, there is some danger of loss of that element (recognized by the peculiar odor) at the moment of incipient fusion. In such cases it is better to mix the ore at first only with the proper amount of sodium carbonate (or sodium potassium carbonate), and heat slowly up to the temperature of sintering. The flux should be dry and well pulverized to permit of intimate admixture. Then add the nitrate to the hot mass, distributing it as evenly as may be over the surface. Raise the temperature slowly to full fusion, and keep it fused for a few minutes. To facilitate cooling and dissolving, pour the melt into a clean platinum dish (dry inside) which is floated on the surface of cold water. After cooling, exhaust with boiling water, filter off the insoluble material, and wash. The solution contains nitrites and carbonates which must be removed by acidification with dilute nitric acid and boiling. It is then rendered *slightly* alkaline with ammonia, and an excess of silver nitrate solution is added. The ammonium nitrate in the solution prevents the separation of any silver as oxide. At this point great care must be exercised to insure the proper conditions for the precipitation of *all* the arsenic as brick red Ag_3AsO_4 ; a few drops each, of very dilute nitric acid, very dilute ammonia, and of silver nitrate solution are added in turn, and the addition of one or the other reagent continued until no further precipitation is produced. It will be remembered that the silver arsenate is soluble in an excess either of nitric acid

or of ammonia, and the solution must be managed accordingly. Canby (*Trans. Am. Inst. Min. Eng.*, XVII., 77) has proposed the use of a cream of zinc oxide in water (free from chlorides) for neutralization in place of the ammonia. The excess of zinc oxide being insoluble gives an advantage, and this modification has met with much favor. On stirring vigorously, and cooling, the precipitate settles rapidly. Filter, and subject the filtrate to tests with dilute nitric acid, ammonia, and silver nitrate solution as before. If any further precipitation is produced, filter again. Then wash until 5 or 10 c. c. of the filtrate gives no more than a faint opalescence with a drop of hydrochloric acid after standing. To determine the silver in the precipitate and conversely the arsenic, some find it convenient to dry the precipitate, add a little "test lead," burn off the paper in a scorifier, cupel the button, and weigh the silver (108 parts Ag = 25 parts As). Usually, however, the Volhard sulphocyanate titration is used. This depends upon the insolubility of silver sulphocyanate in dilute nitric acid. If some ferric salt is present, the characteristic ferric sulphocyanate color will not become permanent until all of the silver has been precipitated.

The strength of the sulphocyanate solution must be in some degree proportioned to the quantities of arsenic with which one has to deal. If they are small, a solution containing 5 gms. of ammonium sulphocyanate per litre may be used. (1 c. c. = approximately 0.0070 gm. Ag or about 0.0015 gm. As.) In the case of ores rich in arsenic a stronger solution may be desirable. The solution is best standardized by dissolving a known weight of pure silver in nitric acid, boiling out the lower nitrogen oxides, adding a few drops of solution of ferric sulphate (or of iron ammonia alum), and titrating until the red color of ferric sulphocyanate is permanent; stir well while adding the sulphocyanate solution. The titration of the silver in the arsenate is performed in a similar manner. Dissolve the precipitate through the filter by the use of warm very

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... til the fumes have no
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an Erlenmeyer flask, fitted with a cork carrying a two-bulb Wurz tube. Rinse into the flask with 20 per cent hydrochloric acid (the ordinary concentrated acid diluted with an equal bulk of water), making the contents of the flask up to about 150 c. c. Add about 5 gms. of ferrous sulphate. Connect the delivery-tube with a condenser, and distil. The arrangement shown in the figure, p. 224, is suitable for the purpose. The form A or B of the receiver may be used. If either antimony or tin is present, the distillation must be interrupted when about half the liquid has been distilled off, and the flask must be filled up to the original volume with 20 per cent hydrochloric acid, when distillation may be resumed. In the absence of antimony or tin there is no danger that the distillate will contain anything other than arsenic, which is precipitable by hydrogen sulphide, and distillation need not be interrupted until the contents of the flask are reduced to a much smaller bulk (30 or 40 c. c.). A fresh quantity of hydrochloric acid must then be added, and the distillation repeated until the distillate gives no precipitate of As_2S_3 with hydrogen sulphide. Unite the distillates, and pass a current of hydrogen sulphide which gives an immediate precipitate of As_2S_3 . Filter, on a weighed filter, wash thoroughly with water, then once or twice with strong alcohol, to remove traces of sulphur and to facilitate drying, and then dry and weigh.

The operation of distilling may be somewhat facilitated by connecting the distilling flask (on the side opposite to the condenser) with a flask containing boiling concentrated hydrochloric acid, the delivery-tube of which dips below the surface of the liquid in the distilling flask.

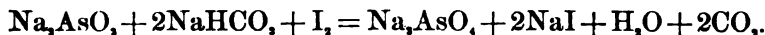
Another method for the examination of minerals containing arsenic consists in decomposing with hydrochloric acid and potassium chlorate as for distillation, diluting, and then without filtering passing hydrogen sulphide rapidly *in the cold* to separate precipitable elements other than arsenic, filtering into a pressure bottle, saturating the filtrate with hydrogen sulphide, stoppering tightly and

heating in a boiling-water bath for an hour, which effects the precipitation of As_2S_3 . This may be filtered off, washed, dried, and weighed. If the hydrogen sulphide in the first treatment is allowed to act too long, or the solution is warmed at that stage, some arsenic will be separated with the mixture of sulphides and undissolved gangue, and consequently be lost. It will therefore always be safe to treat the mixed sulphides and gangue with a little solution of ammonium carbonate. If on acidification the ammonium carbonate solution shows a yellow precipitate of arsenic sulphide, add it to the main precipitate.

Arsenic, when obtained in the pentad form, is sometimes separated for weighing in the form of ammonium magnesium arsenate, corresponding to the phosphorus compound (see Analysis of Magnesium Sulphate, page 28). The conditions necessary for this precipitation, as regards cold alkaline solution, absence of ferric, calcium salts, etc., are essentially the same as in the case of the phosphate. The precipitate is, however, more readily soluble in the agents employed. It is necessary to introduce a minimum of ammonium chloride and of ammonia, and to add to the solution about one third of its bulk of strong alcohol, washing afterward with diluted alcohol containing a little ammonia. The use of alcohol renders the presence of sulphates inadmissible. Magnesium chloride must be used as the precipitant. After obtaining the clean precipitate, it should be dissolved through the filter with dilute nitric acid into a weighed capsule, the solution evaporated to dryness, and very gradually heated up to the temperature of ignition, when it may be weighed as pyroarsenate ($\text{Mg}_2\text{As}_2\text{O}_7$). Drying the compound $\text{MgNH}_4\text{AsO}_4$ at 100° for weighing gives low results, as the salt loses some ammonia of composition even at that temperature. Rapid heating of the precipitate, or heating in contact with reducing agents as burning filter-paper, etc., causes loss of arsenic, but if decomposed by the application of a gradually increasing heat one even-

tually obtains pure pyroarsenate, which is unaffected by the full heat of the Bunsen burner.

Volumetric methods are in many cases applicable for the determination of arsenic. Besides the indirect silver sulphocyanate method already given, the uranium method (used more frequently for phosphoric acid) or the iodine titration in alkaline bicarbonate solution may be used. For the latter the arsenic must be brought to the triad form. This is most conveniently accomplished by mixing the arsenic solution with an equal bulk of strong solution of sulphurous acid, stoppering in a flask, and heating for an hour in a boiling-water bath as for the pentasulphide precipitation. (McCay, *Ch. News*, LI., 122; also, *Am. Chem. Jour.*, VII., 373.) The excess of sulphur dioxide is then boiled out, its expulsion being assisted by the passage of a current of air. The solution is then nearly neutralized with sodium carbonate, and then a slight excess of sodium bicarbonate is added. On adding a few drops of starch solution, it is, if *cold* ready for titration with tenth normal iodine. The iodine solution is made by dissolving 12.7 gms. of pure iodine, together with 18 or 20 gms. of potassium iodide, in a small amount of water, and then diluting to one litre. It will be found that the iodine dissolves comparatively slowly in dilute potassium iodide, so that it will be well to restrict the amount of water used until the iodine has been all taken up. This solution should be standardized by arsenious acid. 4.95 gms. of pure sublimed As_2O_3 is dissolved in sodium or potassium bicarbonate, and diluted to one litre (1 c. c. = 0.00375 As). 10 c. c. or some convenient (measured) quantity of this solution after addition of a little starch is titrated with the iodine solution. The reaction is:



The solution must be sufficiently alkaline to permit this reaction to take place. The end-reaction is the production

of a permanent blue color ("starch iodide") indicating that no more iodine is absorbed in oxidizing the arsenite. The presence of an excess of caustic or monocarbonated alkalis interferes with the end-reaction; it is also prevented by heat. In a cold solution containing alkaline bicarbonate such interference does not occur.

For preparation of the starch solution, see page 207.

NOTE.—It will be observed that the reactions of arsenic and of phosphoric acids are so very similar, that by some methods phosphoric acid, if present, would be estimated with arsenic. In case phosphorus or phosphates are present a separation (best by the use of hydrogen sulphide) becomes indispensable.

CHAPTER XXVIII.

ANTIMONY ORE.

Stibnite (Sb_2S_3) is the principal ore of antimony. The usual method for separating the element consists in converting it into the form of soluble sulphantimonite (or sulphantimonate), which eliminates on the one hand the members of the hydrogen sulphide group (excepting arsenic and tin), and on the other hand the ammonium sulphide group (iron is seldom absent). From the alkaline sulpho-solution antimony sulphide may be separated by acidification. It may be weighed as sulphide, as oxide (Sb_2O_3),* or it may be dissolved and determined by some volumetric method.

To determine antimony in ores, treat 1 gm. of the pulverized material with hydrochloric acid. To avoid loss by volatilization of antimonious chloride, the acid should be somewhat diluted, and the solution should not be allowed to boil. Heating on the water-bath is therefore preferable. Loss by volatilization may also be restricted or prevented by addition of alkaline chloride in sufficient quantity to form a double alkaline antimony chloride (3KCl , SbCl_2 , etc.), from which antimonious chloride volatilizes less readily. The addition of some oxidizing agent, as potassium chlorate or nitric acid, as in the case of arsenic ores, also affords some advantage. This mode of procedure is, however, complicated by the tendency of antimony to form the insoluble oxide Sb_2O_3 under these conditions, which oxide may protect some of the ore from the attack of the

* The constitution of this oxide is not quite certain. It is regarded by some as antimonious antimonate ($\text{Sb}_2\text{O}_3 \cdot \text{Sb}_2\text{O}_5$), "antimonoso-antimonate;" by others as an oxide in which antimony is tetrad (Sb_2O_4 or SbO_2). In some of the older works on chemistry this is called "antimonious acid."

acid, or may be left with the insoluble gangue. This tendency is more marked when nitric acid is used than with potassium chlorate. The action of the oxidizing agent in causing a copious separation of sulphur, which would otherwise escape as hydrogen sulphide, also renders it advisable to avoid the use of oxidizing agents unless the ore cannot be decomposed without them. The addition of 2 or 3 gms. of tartaric acid, while dissolving, although it consumes some of the oxidizing power of the reagent, helps to prevent the formation of Sb_2O_3 at this stage.

After decomposing the ore, add 2 gms. of tartaric acid (to prevent separation of oxychloride on dilution), warm, and dilute to about 80 c. c. Render alkaline with caustic potash and digest a short time to take up Sb_2O_3 , etc., and then add freshly prepared KHS, and digest warm for at least an hour. If copper is absent the corresponding ammonium compounds may be used. This affords the soluble alkaline sulpho-compound. This compound is more readily formed by the use of alkaline polysulphide, but the separation from other metals likely to be present is usually less perfect; moreover, in the next step the antimony sulphide obtained is mixed with much sulphur, which is a disadvantage.

The soluble alkaline sulphantimonite (or sulphantimonate) may also be obtained by the treatment prescribed for tin ore—fusing with sodium or potassium carbonate and sulphur, or with sodium hyposulphite (see Tin ore, Chap. XXV.). Becker (*Fres. Zts. Anal. Chem.*, XVII., 185) prescribed 1 gm. of ore, 3 gms. NaKCO_3 , and 3 gms. sulphur, to be fused together and then extracted with water.

However obtained, filter the antimony solution from the gangue and insoluble sulphides, and digest the insoluble portion with more alkaline sulphide until the solutions afford no separation of orange antimony sulphide upon acidifying. Unite the solutions, and acidify with dilute sulphuric acid. This throws down antimony sulphide, mixed with more or less sulphur. On filtering, washing,

and drying this precipitate approximate results may be obtained. Arsenic, if in the original ore, would be present in this precipitate. It can, however, be removed by washing a few times with solution of ammonium carbonate (after all hydrogen sulphide has been washed off), in which the antimony sulphide is but slightly soluble. For fairly accurate determinations of antimony, certain facts must be taken into consideration. The precipitate (if already in the form of Sb_2S_3) obstinately retains some water unless heated to 200°C . (when it turns black). That temperature will scorch a filter-paper, if maintained sufficiently long for its purpose, so that the precipitate should be collected on something other than paper, as asbestos or sand. It may also contain some free sulphur or some pentasulphide; the sulphur may be removed by treatment with strong alcohol (to take out water), and then washing with carbon disulphide, but this method is unsatisfactory and annoying. The best method is heating in a current of carbon dioxide gas at 200 to 230°C ., which in time will volatilize the free sulphur, also that combined to form pentasulphide, leaving all the antimony as tersulphide.*

A method giving much more satisfactory results consists in converting the sulphide to Sb_2O_3 . This may be accomplished by the action of fuming nitric acid. It is usually recommended that this treatment should be conducted in a capacious porcelain crucible, previously weighed. The proceeding may, however, be facilitated, and loss by spattering more readily avoided, if the precipitated sulphide is transferred to a small beaker, partially dried, and then after conversion to the oxide by fuming nitric acid rinsing into a weighed crucible, drying, igniting, and weighing. All of the sulphur must be oxidized before ignition. In treating with the acid, care must be taken not to heat too high or the sulphur will fuse together in the form of a

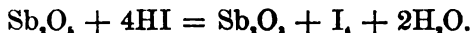
* A form of apparatus adapted for this purpose is figured in *Fres. Zts. Anal. Chem.*, XXXI., 589.

globule, which may enclose and protect some of the antimony compounds, and moreover presents a comparatively small surface for the action of the acid, thus causing vexatious delay. As sulphur melts at a temperature below the boiling-point of nitric acid, the heat must be kept below that point so long as any sulphur is visible. Final ignition is necessary to expel both the excess of nitric acid and the sulphuric acid resulting from oxidation. Ignition in contact with filter-paper, sulphur, or other reducing agent will cause loss of antimony by volatilization.

Another method of obtaining Sb_2O_3 from the sulphide consists in mixing with 30 to 50 times its weight of pure mercuric oxide, and heating cautiously to ignition. Oxygen is thus liberated in contact with the sulphide, and metallic mercury and sulphur oxides are volatilized together. The operation should of course be conducted under a hood.

As regards the separation of arsenic which might accompany the antimony and be estimated with it, one method—treating the sulphides with ammonium carbonate solution—has already been mentioned. Another method consists in the addition of magnesium chloride and ammonia to the solution of the sulphosalts and allowing to stand. If the arsenic is in the pentad form, ammonium magnesium arsenate separates. Still another method is Fischer's distillation process (see Arsenic ore and the precautions necessary when antimony is present). This last is the most accurate.

Of volumetric methods for antimony the iodine processes have met with most favor. In an acid solution containing antimonious acid the addition of hydriodic acid (or potassium iodide which affords hydriodic acid) produces antimonious acid and free iodine, which may be determined. The reaction may be suggested thus:



The similarity to the iodide titration of copper may be noted.

On the other hand, in an alkaline solution of antimonite, the addition of iodine causes the formation of antimonate, a reaction suggested by reversing the above equation, and which is similar to the iodine titration for arsenic (see arsenic ore). The solution is prepared for titration very much in the same manner. Sodium sulphite or sulphurous acid is added to the acid solution, which is then boiled to expel the excess of sulphurous acid—facilitated by passing a current of air or of carbon dioxide through it. Tartaric acid is then added, and the solution is neutralized with sodium carbonate; some bicarbonate is added, then starch, and the titration conducted with tenth normal iodine which has been standardized with pure arsenious acid. The antimony standard of the iodine solution as compared with the arsenic standard is in the ratio of their atomic weights (120 : 75); *e. g.*, if the iodine solution is exactly tenth normal (1 c. c. = 0.00375 gm. As), it will be for antimony, 1 c. c. = 0.0060 Sb.

CHAPTER XXIX.

LEAD—ANTIMONY ALLOYS (TYPE METAL).

The metals to be looked for are antimony, lead, tin, copper, and iron; arsenic and zinc may also be present.

To 1 gm. of the metal, comminuted by drilling, shaving, or filing, add 3 or 4 gms. of tartaric acid, and 20 c. c. of dilute nitric acid, prepared by mixing 1 part of concentrated nitric acid with 2 parts of water. Digest on a water-bath until excess of nitric acid is entirely expelled, add 50 c. c. of water, excess of ammonia, 10 c. c. of yellow potassium sulphide, and allow to stand on a water-bath for 3 or 4 hours, the water in the bath being heated to a point just below boiling. Do not heat strongly. Dilute to about 100 c. c., filter, and wash with water until the washings are colorless. The oxides of antimony and tin go into solution as potassium sulphantimonate and sulpho-stannate, while the lead and iron sulphides remain on the filter undissolved. Wash the contents of the filter, dry the filter, burn it in a porcelain crucible, after moistening with nitric acid, add to the ash 5 or 6 drops of nitric acid, warm, and wash it into the casserole. Then add 6 or 7 c. c. of nitric acid and 2 or 3 c. c. of sulphuric acid, and heat until fumes of SO_2 appear; cool, add 50 c. c. of water, filter, and wash with 40 or 50 c. c. of water containing 1 per cent of sulphuric acid. Dry the filter and contents, transfer the latter to a clock-glass, place the filter in a capacious weighed porcelain crucible, add 8 or 10 drops of nitric acid and 4 or 5 drops of sulphuric acid, evaporate off the excess of acid, and ignite. Again add 4 or 5 drops of nitric acid and 1 or 2 drops of sulphuric acid, expel excess of acid, transfer the contents of the filter from the clock-glass to the crucible, ignite all,

cool, weigh the lead sulphate, and calculate the per cent of lead. (Consult analysis of galena.)

Acidify the alkaline filtrate containing the tin and antimony, and perhaps some arsenic, with hydrochloric acid, and allow the sulphides to settle in a warm place, avoiding great heat. Then filter, wash with water, displace the water with a little alcohol, dry at a moderate heat, run a little carbon disulphide through the filter, to dissolve out free sulphur, expel excess of carbon disulphide at gentle heat (better in a steam-bath), place the filter and contents in a large porcelain crucible, add 1 or 2 c. c. of nitric acid, and cover with a glass. When the violent action is over, add 4 or 5 c. c. of red fuming nitric acid, and evaporate at a gentle heat nearly to dryness to convert the sulphides into oxides. Then neutralize the remaining acid with pure sodium hydrate, wash the oxides into a silver dish with water containing a little sodium hydrate (using as little as possible), evaporate nearly to dryness, add about 8 parts of pure sodium hydrate, and a little sodium nitrate, continue the evaporation to perfect dryness, and fuse. As soon as the mass is fused, remove the heat, and when it is cool enough add 100 c. c. of hot water, and boil until the contents of the dish are pulverulent. Finally, cool, add alcohol to the amount of one third the volume of the fluid, filter, wash the residue with dilute alcohol (prepared by mixing 1 part of alcohol with 2 parts of water), to which has been added a few drops of strong solution of sodium carbonate. The insoluble sodium antimonate will remain on the filter, while the sodium stannate and sodium arsenate go into solution. Wash the antimonate from the filter into a beaker with water, place the beaker under the filter, and pour through the latter 10 or 15 c. c. of warm concentrated hydrochloric acid, containing 1 gm. of tartaric acid, wash with a little water, and warm until everything is dissolved. Dilute the solution to 100 c. c., saturate it with sulphuretted hydrogen, filter, wash, treat the precipitate as directed in the analysis of antimony ore,

and calculate the per cent of antimony. (See *Fres., Quant. Anal.*, § 165—4—a.)

Should there be no arsenic present, acidify the filtrate containing tin with hydrochloric acid, and saturate with sulphuretted hydrogen. Heat, filter, wash with solution of ammonium acetate, containing a little free acetic acid, dry, roast at gentle heat in a weighed porcelain crucible, then heat strongly, cool, weigh the stannic oxide, and calculate the per cent of tin. (See analysis of tin ore.) Purify the weighed precipitate as in analysis of bronze. Should arsenic be present, it will be found, together with the tin, in the filtrate from the sodium antimonate, after the fusion with sodium hydrate. Add to the filtrate 1 or 2 c. c. of ammonia, and 2 or 3 c. c. of yellow ammonium sulphide, and warm gently for a short time. Then add 2 c. c. of "magnesium mixture," and allow to stand for 12 hours. Filter out the magnesium-ammonium arsenate, and wash. Arsenic is usually small, and is best determined by the distillation method (see Chapter XXVII.).

Acidify the filtrate from the magnesium arsenate with hydrochloric acid, precipitate the tin as sulphide, and proceed to determine it as directed above.

The filtrate from the lead sulphate will contain the copper, zinc, iron, etc., and should be treated for the determination of those metals (see Chapter XXVII.).

Clarke's method for separating tin from antimony may be found more convenient than the soda fusion method. It depends upon the use of hot solution of oxalic acid in which stannic sulphide is soluble, whereas antimony sulphide is insoluble, provided an excess of hydrogen sulphide is present.

The solution of potassium (or ammonium) sulphantimonate and sulphostannate, obtained as described, is slowly poured into a boiling solution of oxalic acid, enough of that acid being used, to leave a decided excess when all of the solution of alkaline sulphosalt has been added. Then boil for about ten minutes, at the same time passing

hydrogen sulphide through the solution. The precipitate, consisting chiefly of antimony sulphide, is filtered off, redissolved in ammonium sulphide, and the operation repeated, which usually affords antimony sulphide entirely free from tin. Treat the precipitate with nitric acid, etc. (see Antimony ore).

The combined filtrates containing the tin are neutralized with ammonia, then acidified with acetic acid, and hydrogen sulphide passed in to precipitate stannic sulphide, insoluble in neutral oxalates or in acetic acid. The precipitate is handled as described (see Tin ore, also Bronze, Chapters XXV. and XXVI.).

REFINED LEAD.

For other metals, dissolve 200 gms. in nitric acid. *Note 2.*

Compare Fres., *Zeit. für An. Chem.*, Vol. VIII., 1869. The lead may contain silver, copper, bismuth, cadmium, zinc, iron, nickel, cobalt, arsenic, antimony, tin, manganese.

Note 1.—The silver may be determined either by cupellation, or by a wet method. If the latter plan is adopted, weigh 200 gms. of pieces, scraped clean, introduce them

into a 1.5-litre flask, add nitric acid of 1.2 sp. gr., in small portions at a time, always keeping the metal in excess, and heat the liquid until only about 5 or 10 gms. of lead remain undissolved, and the solution begins to turn yellow in consequence of the formation of lead nitrite. The silver will be concentrated in the residual metal. Withdraw it from the solution, and dissolve it in nitric acid, dilute to 200 c. c., and add a mixture of 1 c. c. of hydrochloric acid and 50 c. c. of water. Allow the whole to stand 2 or 3 days, and after all the silver chloride has settled, draw off the clear fluid, and filter out the silver chloride, on a small filter, wash with hot water, dry, and ignite filter and precipitate together in a small weighed porcelain crucible. If the amount of silver chloride is so considerable that there is a possibility of its being incompletely reduced by the combustion of the filter-paper, the residue must be heated for a few minutes in a stream of hydrogen before weighing. The amount left, after subtracting the filter-ash, gives the quantity of silver in the 200 gms. of lead. The refined metal seldom contains more than 0.0015 per cent of silver.

Instead of treating the ignited precipitate with hydrogen, add about 0.5 c. c. of nitric acid, evaporate to dryness, again add 0.5 c. c. of nitric acid, heat to dissolve any reduced silver, add 8 or 10 drops of hydrochloric acid, evaporate to dryness, fuse the silver chloride, cool, weigh, and calculate the silver. (See analysis of barium chloride.)

Note 2.—For the main analysis, weigh 200 gms. of lead, cleaned as before, introduce it into a 2-litre flask, add 500 c. c. pure nitric acid of 1.2 sp. gr. and 1 litre of water, and allow it to stand for 24 hours. Should a residue (*a*) containing antimony and tin remain, filter it out, dissolve it in hydrochloric acid, dilute a little, pass sulphuretted hydrogen through the solution, filter out the precipitate, wash, and reserve it to go with precipitate (*r*), consisting of the sulphides of antimony, arsenic, and tin.

Note 3.—Transfer the clear solution (*a*) to the 2-litre flask,

if not already there, add 65 c. c. of pure concentrated sulphuric acid, shake, cool, fill up to the 2-litre mark, agitate again, and allow to settle. Then siphon off accurately 1750 c. c. of the clear solution, and reject the rest containing lead sulphate or residue (*b*). It has been found, by repeated experiments, that the lead sulphate from 200 gms. of lead occupies 44.99 c. c., or, in round numbers, 45 c. c. The 2-litre flask, when filled to the mark, will hold, then 1955 c. c. of solution and 45 c. c. of lead sulphate. But as 1955 c. c. of the solution correspond to 200 gms. of the lead, then 1750 c. c. of solution will correspond to 179.03 gms. of the original lead, or, in round numbers, 179 gms. Consequently, all the calculations must be based upon this as the quantity taken for analysis. Evaporate the 1750 c. c. of solution (*b*), to fumes of SO_3 , allow to cool, add 60 c. c. of water, filter off and wash precipitate (*c*) of lead sulphate, containing, perhaps, a little antimony.

Note 4.—Dissolve precipitate (*c*) in hydrochloric acid, add 10 volumes of sulphuretted hydrogen water, warm, pass sulphuretted hydrogen gas, allow the precipitate to settle, filter, wash, spread filter in a porcelain dish, heat with a solution of yellow sulphide of ammonium or potassium, to which a little pure sulphur has been added, filter, wash, acidify the filtrate with hydrochloric acid, allow the precipitate to settle at a gentle heat, filter, and wash.

Reject the filtrate, or filtrate (*d*), and add the precipitate, or precipitate (*d*), to precipitate (*f*). If precipitate (*d*) contains much lead, treat it again with ammonium or potassium sulphide, as before, filter, acidulate with hydrochloric acid, allow the antimony sulphide to settle, filter, and add the pure antimony sulphide to precipitate (*f*).

Note 5.—Dilute solution (*c*), the filtrate from precipitate (*c*) of lead sulphate, to 200 c. c., heat to 70°C ., pass the sulphuretted hydrogen, allow to stand 12 hours over a very gentle heat, filter through a small filter, and wash with hot water. There will be a solution (*f*), which may contain iron, zinc, cobalt, nickel, and manganese, and a

precipitate (*f*), which may contain antimony, arsenic, tin, bismuth, copper, cadmium, and lead.

Note 6.—Evaporate solution (*f*) to a volume of about 400 c. c., transfer to a half-litre flask, make alkaline with ammonia, mix with freshly-prepared ammonium sulph-hydrate, fill the flask, and allow to stand 24 hours. When the precipitate (*g*) has settled, filter, acidify the filtrate, or solution (*g*), with acetic acid, and boil to recover any nickel which may have been retained in the solution. Filter out precipitate (*k*) of nickel sulphide, and, after washing it slightly and drying, add it to precipitate (*g*), which contains the principal part of the nickel, and reject the filtrate, or solution (*k*).

Note 7.—Treat precipitate (*g*), containing, perhaps, iron, zinc, nickel, cobalt, and manganese, on the filter, with a mixture of 1 part of hydrochloric acid of sp. gr. 1.12, and 6 parts of sulphuretted hydrogen water, pouring back the filtrate repeatedly on the filter, to avoid increasing the volume of fluid unnecessarily. Burn the filter containing residue (*h*), after drying, together with the filter, containing precipitate (*k*), in a porcelain crucible, treat with nitro-hydrochloric acid, concentrate the solution, add a little water, filter, wash, make the filtrate alkaline with ammonia, add a few drops of ammonium carbonate, filter into a platinum dish, treat the filtrate with a few drops of strong solution of potassium hydrate, and heat until ammonia is entirely expelled. Then filter off the slight flocculent precipitate, wash, dry, ignite, and weigh the nickel oxide, and calculate metallic nickel. (See analysis of nickel ore.) Test the precipitate with the blow-pipe for cobalt.

Note 8.—Add a few drops of nitric acid to solution (*h*), containing the iron and zinc, concentrate, make alkaline with ammonia, filter off the ferric hydrate, or precipitate (*i*), dissolve the precipitate with a few drops of hydrochloric acid, again precipitate with ammonia, filter, wash, dry, ignite, weigh the ferric oxide, and calculate metallic iron. To verify the results, fuse the precipitate with acid

sodium sulphate, dissolve in water, reduce with zinc and platinum, and determine the iron with a dilute solution of potassium permanganate. (See analysis of ammonia-iron-alum.)

Note 9.—Mix solution (*i*), or the filtrate from the ferric hydrate, with a little ammonium sulph-hydrate in a small flask, and allow to stand for 24 hours in a warm place. Filter out precipitate (*j*), wash and digest on the filter with dilute acetic acid, to dissolve out any manganese sulphides. Dissolve the residue of zinc sulphides remaining on the filter with hydrochloric acid, boil, after adding a little potassium chlorate to oxidize the sulphur, precipitate the zinc with sodium carbonate, and from the ignited precipitate calculate the zinc. (See analysis of zinc ore.)

Boil solution (*j*), or the acetic acid solution of manganese sulphide, to small volume, add a little bromine water, warm until the excess of bromine is expelled, filter, wash with hot water, dry, ignite the precipitate, and calculate the manganese. (See analysis of manganese ore.)

Note 10.—Heat precipitate (*f*), which may contain antimony, arsenic, tin, copper, bismuth, cadmium, and lead, after adding precipitate (*f*), with a solution of potassium sulphide, to which some pure sulphur has been added, filter out residue (*l*), which may contain bismuth, copper, cadmium, and lead, and wash with hot water. Acidulate the filtrate, or solution (*l*), which may contain arsenic, antimony, and tin, with hydrochloric acid, and allow the precipitate to settle completely. Filter out precipitate (*r*), which may contain arsenic, antimony, and tin, and reject the filtrate, or solution (*r*).

Heat residue (*l*), (insoluble in potassium sulphide) nearly to boiling, in a porcelain dish, with dilute nitric acid (prepared by mixing 1 part of acid of 1.2 sp. gr. with 12 parts of water). When the precipitate is dissolved, filter, wash the paper slightly, dry, ignite it, and add the ash to the nitric-acid solution. Then add 2 c. c. of dilute sulphuric acid, evaporate to fumes of SO_3 , dilute a little, and filter

out and wash precipitate (*m*) of lead sulphate, which may be rejected. (See analysis of galena.)

Note 11.—Nearly neutralize solution (*m*) (or the filtrate from the lead sulphate, and which may contain bismuth, copper, cadmium, and silver), with pure potassium hydrate, add Na_2CO_3 and a little of a solution of pure potassium cyanide free from potassium sulphide, and heat gently. If a precipitate (*n*) of bismuth hydrate is produced, filter it out, wash, dissolve it in dilute nitric acid, precipitate it with ammonium carbonate, weigh it as bismuth trioxide (Bi_2O_3), and calculate the metallic bismuth. (See *Fres., Quant. Anal.* § 120.) To solution (*n*) add a little more potassium cyanide and a few drops of potassium sulphide, filter and wash the precipitate (*o*) of sulphides of cadmium and silver, dissolve in dilute nitric acid, add a little hydrochloric acid, filter out and wash the precipitate of silver chloride or precipitate (*x*), which may be rejected, as the silver is determined elsewhere. Evaporate solution (*x*), containing cadmium, nearly to dryness, add a few drops of solution of sodium carbonate, filter out the precipitate of cadmium carbonate, wash, dry, ignite, and weigh the cadmium oxide, and from it calculate metallic cadmium. To prevent reduction and volatilization of cadmium during the ignition, moisten the filter with solution of ammonium nitrate.

If no precipitation of the cadmium is produced by the sodium carbonate, add a little potassium hydrate, and if one then forms, filter, wash, and proceed as above. Mix the filtrate from the sulphides of silver and cadmium, or filtrate (*o*), with a small quantity of nitric and sulphuric acids, and evaporate nearly to dryness. Then add a few drops of hydrochloric acid, and heat until cyanogen is expelled. Filter, if necessary, and determine the copper by one of the methods given in the analysis of copper ore.

When cadmium is absent, the separation of the bismuth and copper may be effected by means of ammonia and ammonium carbonate, removing any silver by hydrochloric

acid before precipitating copper sulphide. (For precautions to be observed, see Fres., *Quant. Anal.*, § 163, 5.)

Note 12.—To precipitate (*r*), which may contain arsenic, antimony, and tin, and which was obtained by acidifying the potassium sulphide solution (*l*) with hydrochloric acid, add the sulphuretted hydrogen precipitate from the solution of residue (*a*), (see *Note 2*), dry, and treat repeatedly with carbon disulphide. After the carbon disulphide has evaporated from the filter, warm it, with its contents, in a covered porcelain crucible, after adding a few drops of red fuming nitric acid, heat the solution cautiously to expel excess of nitric acid, add sodium carbonate in excess and a little sodium nitrate, evaporate to dryness, and heat until the mass melts, and becomes white. Transfer the fused mass to a small mortar, add a little water, and pulverize carefully. Then wash it into a breaker, and proceed as directed in the analysis of type metal. (See also Fres., *Quant. Anal.*, page 427.)

Dissolve residue (*s*) of sodium antimonate, in hydrochloric and tartaric acids, pass sulphuretted hydrogen, set aside for a few hours, filter out antimony sulphide, wash, dry the precipitate, and reserve it to be combined with the sulphuretted hydrogen precipitate from the solution of residue (*u*).

Evaporate solution (*s*), which may contain arsenic, antimony, and tin, in order to expel alcohol, add excess of dilute sulphuric acid, evaporate to expel nitric acid, add water, heat to 70° C., and pass sulphuretted hydrogen. When precipitate (*t*) has settled, filter, and wash with water, and reject the filtrate, or solution (*t*). If no tin be present, treat precipitate (*t*), on the filter, with a cold concentrated solution of ammonium carbonate, pouring the filtrate back on the filter repeatedly in order to avoid the use of a large excess of solution of ammonium carbonate. The ammonium carbonate solution (*u*) will contain the arsenic. Acidulate it with hydrochloric acid, add a little filtered sulphuretted hydrogen water, filter through a

small tube, in which a little asbestos has been placed, both having been previously heated and weighed. When the whole of the precipitate has been transferred to the little tube, heat it at 100°C. , until the greater portion of the water is expelled, and then heat it gently, not much above 100°C. , in a stream of dried carbon dioxide, allow it to cool in a current of the gas, displace the carbon dioxide with atmospheric air, and weigh the tube and contents, and, from the trisulphide, calculate the arsenic. A better plan is to filter out the arsenious sulphide on a very small filter, oxidize the filter and sulphide together by evaporation with fuming nitric acid, fuse the residue in platinum with a little sodium carbonate and nitrate, dissolve in water, and weigh the arsenic as magnesium pyro-arsenate, as directed in the analysis of arsenic ore.

Note 13.—Dissolve residue (*u*) containing antimony, together with the precipitate from solution of residue (*s*), in strong hydrochloric acid, pass sulphuretted hydrogen, filter through a small tube in the same way as directed above in the case of arsenic, heat gently in a stream of dried carbon dioxide, until the antimony trisulphide turns black, cool in a current of the gas, displace the latter by a current of dry air, weigh the tube and contents, and calculate the antimony. Or, oxidize the antimony oxide by Bunsen's method with nitric acid, and weigh it, as directed in the analysis of antimony ore, as antimony tetroxide.

Note 14.—If tin be present, after expelling alcohol, passing sulphuretted hydrogen, and filtering out the precipitate, dissolve the latter in potassium sulphide, add excess of sulphurous acid, digest for some time on a water-bath, and then boil until two thirds of the water, and all the sulphurous acid are expelled. Solution (*t*) will contain all the arsenic. (See Bunsen, in *Annal. d. Chem. u. Pharm.*, 106, 3, and Fres., *Quant. Anal.*, § 165-6.)

Precipitate the arsenic as sulphide, oxidize, fuse, take

up with water, and weigh the arsenic as magnesium pyroarsenate, as directed in the analysis of arsenic ore.

Residue (*f*) will contain the tin and antimony. Oxidize it with fuming nitric acid in a weighed porcelain crucible, and weigh. Then ignite in a stream of hydrogen to expel the antimony tetroxide, oxidize again with nitric acid, and weigh the stannic oxide, from which calculate the tin. Calculate the antimony from the loss of antimony tetroxide. The tin and antimony may be separated and determined by oxidizing the residue left after extracting the arsenic, with nitric acid, fusing, dissolving in water, filtering out the soluble stannate from the insoluble antimonate, which latter is to be dissolved in hydrochloric and tartaric acids, precipitated as sulphide, and the sulphide oxidized and weighed as antimony tetroxide, as directed in the analysis of antimony ore.

To determine the tin, precipitate the sulphide from the solution of stannate, by means of sulphuretted hydrogen, filter it out, and burn it to stannic oxide, as directed in the analysis of tin ore.

Note 15.—To determine the small quantity of sulphur which may be present in the lead, draw out a piece of combustion tubing about 1 metre long, and of about 2 centimetres diameter, to a long point, which is bent down so as to dip into a small 3-bulbed U tube filled with water. Also narrow the combustion tube in the middle, so as to form a kind of bridge. Introduce into the anterior end of the tube about 100 gms. of the lead, in the form of a rod of about 1 centimetre diameter, close the tube with a common cork, connect it with a smaller tube containing fragments of charcoal, and place it in a combustion furnace. Then heat the charcoal to the point of ignition, and pass a current of chlorine. When the tubes are filled with chlorine, melt the lead carefully, the tube being so inclined that the melted lead will flow against the bridge, but not over it, and not flow back against the cork. Keep the charcoal red hot to remove any oxygen from the

chlorine. Regulate the heat so that the lead will burn slowly to lead chloride, and collect in the empty part of the tube. If the stream of chlorine is properly regulated, and the lead chloride not heated, very little of it will pass over into the U tube. Wash the contents of the U tube into a beaker, precipitate the SO_2 with barium chloride as usual, and calculate the sulphur.

CHAPTER XXXI.

WHITE PAINT GROUND IN OIL.

Extract the oil. *Note 1.* The dry paint may contain BaSO_4 , PbSO_4 , CaSO_4 , 2PbCO_3 — PbH_2O_2 , BaCO_3 , CaCO_3 , ZnO , PbO , SiO_2 , $\text{Al}_2(\text{SiO}_3)_3$. *Note 2.*

<i>Residue (a).</i>		<i>Solution (a).</i>	
BaSO_4 , PbSO_4 , CaSO_4 , SiO_2 , $\text{Al}_2(\text{SiO}_3)_3$. <i>Note 3.</i>		$\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$, $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2$, $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$, $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$. <i>Note 9.</i>	
<i>Residue (b).</i>	<i>Filtrate (b).</i>	<i>Precipitate (e).</i>	<i>Filtrate (e).</i>
BaSO_4 , PbCO_3 , CaCO_3 , SiO_2 , $\text{Al}_2(\text{SiO}_3)_3$. <i>Note 4.</i>	$(\text{NH}_4)_2\text{SO}_4$. It may be rejected. <i>Note 3.</i>	PbS , ZnS . <i>Note 9.</i>	$\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$, $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$. <i>Note 11.</i>
<i>Residue (c).</i>	<i>Solution (c).</i>	<i>Res. (f).</i>	<i>Filt. (f).</i>
BaSO_4 , SiO_2 , $\text{Al}_2(\text{SiO}_3)_3$. <i>Notes 5 and 6.</i>	$\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$, and $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$. <i>Note 7.</i>	PbSO_4 . <i>Note 9.</i>	ZnSO_4 . <i>Note 10.</i>
<i>Precipitate (d).</i>	<i>Solution (d).</i>	<i>Prec. (g).</i>	<i>Filt. (g).</i>
PbS . <i>Note 7.</i>	$\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$. <i>Note 8.</i>	BaSO_4 . <i>Note 11.</i>	$\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$. <i>Note 12.</i>

The paint may contain, besides the oil, one or more of the following constituents, namely: Sulphates of lead, barium, and calcium; carbonates of lead, barium, and calcium; oxides of lead and zinc, and also silica and clay.

Make a careful qualitative analysis of the paint, after extracting the oil, for upon it will depend the character of the quantitative analysis.

Note 1.—Weigh a clean dry flask, which holds about 150 c. c., and introduce into it 3 or 4 gms. of the paint, and note the weight. Then add 30 or 40 c. c. of ether or gasoline, shake well, and heat over steam until the fluid boils. Allow the solid matter to settle, and decant the clear fluid on a dry filter without disturbing the residue more than is necessary. Repeat the operation with 25 or 30 c. c. of the solvent. Finally, wash the contents of the

flask on the filter with 25 or 30 c. c. of ether or gasoline, and dry the filter and contents, in an air-bath, at 100° C. The quantitative analysis may be made of a portion of this.

To determine the oil, evaporate the filtrate in a weighed dish, without application of heat, until only oil is left, and then in an air-bath, at a temperature of 100° C., for about an hour, cool, and weigh. Should there be any water in the oil, as there may be, if the ether used was not perfectly anhydrous, continue to heat at 100° C. until it is expelled, and then cool and weigh. Should the filtrate be turbid, and not cleared by refiltering, as is sometimes the case, pour it into a measured flask, dilute to a known volume, dilute with ether or gasoline, as the case may be, cork, and set it aside. After the solid matter has settled, take an aliquot portion of the clear fluid, evaporate it in a weighed dish, as directed above, and calculate the per cent of oil. The proportion of solid matter will be too small to render it necessary to make the allowance for its volume, as in the case of refined lead.

Note 2.—Weigh carefully 1 gm. of the dry residue, from which the oil has been thoroughly extracted, and dissolve it in about 25 c. c. of hot acetic acid, in a covered vessel. Filter, and wash with hot water.

If there be any residue (*a*) left on the filter, it will contain the silica and clay, and sulphates of barium calcium and lead, that may be present in the paint.

Solution (*a*) may contain lead, zinc, calcium and barium in the form of acetates, the last being due to the use of witherite (barium carbonate).

Note 3.—Treatment of residue (*a*):

Wash it from the filter into a beaker with water, add 8 or 10 gms. of ammonium carbonate, plug the point of the funnel, and fill also with a strong solution of ammonium carbonate, placing it in a filter-stand over the beaker, and allow all to stand for 12 hours, with frequent stirring. By this means, the sulphates of lead and calcium will be

converted into carbonates, while the barium sulphate, silica, and clay will remain unaltered. Then remove the plug from the point of the funnel, allow the fluid in the filter to run through into a second beaker, pour the solution of ammonium carbonate, from the first beaker, on the same filter, also transfer to it residue (b) (which may contain sulphate of barium, carbonates of calcium and lead, and silica and clay), and wash well with hot water. The filtrate and washings, or filtrate (b), will contain the sulphuric acid, which was combined with calcium and lead, and may be rejected. (See note on galena analysis, p. 212.)

Note 4.—Pour through the filter containing residue (b) (or the carbonates of calcium and lead, the sulphate of barium, and the silica and clay), hot acetic acid until it produces no effervescence, and wash well with water.

Residue (c) will contain any sulphate of barium, silica, and clay, while filtrate (c) will contain any acetates of lead and calcium.

Note 5.—Dry, ignite, and weigh residue (c). Then fuse it with sodium carbonate, boil the fused mass in water, filter, and wash out alkaline sulphate. Treat the residue, containing barium carbonate, with hot dilute hydrochloric acid, by pouring it through the filter, and wash the latter well with hot water, allowing the filtrate and washings to run together into a separate beaker. To the clear acid solution add sulphuric acid, and determine the barium sulphate as usual. This will give the amount of *barytes* in the paint. The difference between this weight and that of the total residue (c) will give the amount of silica and clay.

Note 6.—Evaporate nearly to dryness the filtrate from the barium sulphate, after washing into it any residue left upon the filter, after dissolving the barium carbonate, transfer to a platinum crucible, add some acid sodium sulphate, and fuse. When the mass is cool enough, add a little sulphuric acid, heat until the mass is brought to a pasty consistence, cool, and dissolve in water. By this

means, the silica will be rendered insoluble, and the alumina dissolved. Filter out and weigh the silica; precipitate the alumina with ammonia, and determine it as usual. Calculate the alumina to clay ($\text{Al}_2(\text{SiO}_3)_2$). Any excess of silica is probably due to the use of infusorial earth.

Note 7.—Saturate the filtrate from the barium sulphate, clay, and silica, or acetic acid solution (*c*), with sulphuretted hydrogen, filter out the lead sulphide, or precipitate (*d*), and wash it with a little sulphuretted hydrogen water. Then wash the precipitate from the filter into a beaker, dry the filter, transfer it to a porcelain crucible, moisten it with nitric acid, burn it, add the ash to the precipitate, and dissolve all with nitric acid. Then add a little concentrated sulphuric acid, evaporate to fumes SO_3 , dilute, filter out, and determine the lead sulphate existing as such in the paint. (See analysis of galena.)

Note 8.—Boil out the sulphuretted hydrogen from the filtrate from the lead sulphide, or solution (*d*), which may contain calcium acetate, add excess of ammonia and ammonium oxalate, filter, treat the precipitate as directed in the analysis of calcite, and weigh the calcium sulphate which existed in the paint as such.

Note 9.—Treatment of solution (*a*):

Solution (*a*) may contain acetates of lead, zinc, calcium, and barium. Saturate with sulphuretted hydrogen, filter out, and wash precipitate (*e*), which may contain sulphides of lead and zinc, dissolve the precipitate in nitric acid, add sulphuric acid to the solution, evaporate to fumes of SO_3 , dilute, filter out the lead sulphate, or residue (*f*), observing the directions given in the analysis of galena, and calculate to basic carbonate of lead ($2\text{PbCO}_3, \text{PbH}_2\text{O}_2$). (See *Note 13*.)

Note 10.—From filtrate (*f*), the filtrate from the lead sulphate, precipitate the zinc with excess of sodium carbonate, or as zinc ammonium phosphate (see analysis of Zinc ore).

After precipitating, and filtering out the zinc carbonate, treat the filtrate with sulphuretted hydrogen, to insure

the complete precipitation of the zinc. Should any zinc sulphide be precipitated, dissolve it in hydrochloric acid and potassium chlorate, precipitate with excess of sodium carbonate or as phosphate, and on obtaining the amount of zinc oxide, add it to the first.

Note 11.—To the filtrate from the sulphides of lead and zinc, or filtrate (*e*), which may contain acetates of calcium and barium, add a little hydrochloric acid, and dilute sulphuric acid, to precipitate any barium present, filter out the barium sulphate, and wash it with sodium hyposulphite, to dissolve out any calcium sulphate which may possibly be present. Weigh the barium sulphate, and calculate it to barium carbonate.

Note 12.—To the filtrate from barium sulphate, or filtrate (*g*), add excess of ammonia, and a sufficient quantity of solution of ammonium oxalate, filter wash, dry, convert the calcium oxalate into sulphate as directed in the analysis of calcite, and calculate to calcium carbonate.

Note 13.—In case there should be any lead oxide in the paint not combined with carbonic or sulphuric acid, it will be in the acetic acid solution (*a*), in which case a careful determination of the carbonic acid must be made, and, after subtracting enough to satisfy the calcium existing as calcium carbonate, the remainder should be calculated to basic carbonate of lead. Should there be any lead left unsatisfied, it is to be calculated to lead oxide. It must be remembered, however, that lead sulphate is slightly soluble in acetic acid, and a slight excess of lead in solution (*a*) may be due to this cause.

Appendix 1.—If the qualitative analysis shows the absence of sulphates of barium, lead, and calcium, should there be any residue left, after dissolving the paint in acetic acid, dry, ignite, and weigh it, as it is probably silica or clay, or both. Then fuse it with acid sodium sulphate, digest the fused mass with sulphuric acid, dissolve in water, filter out the silica, and in the filtrate determine the alumina, and calculate the clay and free silica as in *Note 6*.

If no silica or clay, or sulphates of barium, lead, or calcium be present, acetic acid will dissolve the paint to a clear solution, for the analysis of which proceed as directed in *Notes* 9, 10, 11, and 12.

If no silica, or clay, or salts of calcium and barium be present, but only carbonate of lead and oxide of zinc, the paint may be dissolved in dilute nitric acid, and the solution, after adding sulphuric acid, treated for lead, as directed in analysis of galena; the lead calculated to basic carbonate (white lead), and the zinc precipitated from the filtrate by sodium carbonate, determined as in the analysis of zinc ore, and calculated to oxide.

If the paint be a pure lead paint, dissolve in nitric acid, and determine the lead by evaporating with sulphuric acid, and proceeding as directed in the analysis of galena. The lead is to be calculated to basic carbonate.

If it be a simple zinc paint, dissolve in nitric acid, precipitate the zinc directly with sodium carbonate, and weigh it as oxide, or separate as phosphate. (See Zinc Ore.)

In all cases where zinc is precipitated by sodium carbonate, treat the filtrate with sulphuretted hydrogen, and if any zinc sulphide be recovered, filter it out, dissolve in hydrochloric acid, precipitate with sodium carbonate, and add the precipitate to the first one.

Appendix 2.—In paint composed of sulphate and oxide of lead, and containing no carbonate, after dissolving in acetic acid, filtering, and washing well, dry, ignite as directed in analysis of galena, and weigh the lead sulphate.

In the acetic acid solution, determine both the lead and sulphuric acid, as a small amount of lead sulphate may be dissolved by the acetic acid. Calculate the sulphuric acid to lead sulphate, and add it to that found in the residue. Deduct the amount of lead due to lead sulphate, from the total lead found in the acetic acid solution, and calculate the remainder to lead oxide (PbO), existing as such in the paint.

NOTE.—The white lead of commerce has usually, but *not always*, the composition $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$. Some pigments are now to be found in the market containing basic lead sulphates or chlorides, so that PbO , found as in *Appendix 2*, may be in combination, and in that condition fail to impart any yellow tinge.

In analyzing white paint, the object is usually to determine what substances have been mingled to produce it. The treatment with acetic acid or other solvents may induce the formation of compounds other than those originally used, e.g., if the pigment contains calcium sulphate and lead in some form soluble in acetic acid (carbonate, basic salt, etc.), some lead sulphate not present as such in the original, may be formed. Digestion with cold water will serve *qualitatively* for the detection of calcium sulphate in the mixture. Of course in a white paint purporting to be "white-lead paint" all substances other than basic lead carbonate are regarded as adulterations.

A determination of the percentage of carbonic acid in a pigment may be necessary, as a guide in the estimation of its constituents. The method by direct weight is preferable, though that by loss is sometimes used. (See Calcium Carbonate.)

CHAPTER XXXII.

FRESH WATER.

The kind of analysis required depends upon the use to be made of the water, whether for drinking and general domestic purposes, for steam boilers, for manufacturing purposes, or as a mineral water.

The determination of its value as a potable water can be made by a short and simple analysis, showing the amount of silica, alumina, and oxide of iron, lime, magnesia, soda, potash, chlorine, sulphuric acid, organic and volatile matter (expelled by ignition from the residue left after evaporating a given quantity of water), and ammonia, both free and in a form styled albuminoid, which latter is thought to indicate constituents very detrimental to health. Besides, it is important to know its hardness, or soap destroying power.

This analysis will furnish all the information that is requisite to estimate the fitness of water for use in steam boilers, and for manufacturing purposes.

The analysis of mineral water is much more complicated and laborious, and will be described later.

Total Solids, Organic and Volatile Matter.—Evaporate 100 c. c. of the water in a weighed platinum dish over a water-bath. Finally dry in an air-bath at 120° to 130° C., cool and weigh. The use of a smaller quantity of the water will not, in many instances, give a sufficient amount of solids to make the determination satisfactory, and with larger quantities other conditions, as the advent of dust, etc., will tend to render the results less accurate. The increase in weight of the dish represents *Total Solids*. If the water contains calcium chloride or other hygroscopic salts, it will be found exceedingly difficult to obtain a constant weight.

Then ignite the solids at a low-red heat, holding the burner in the hand, removing the flame momentarily, when the dish shows visibly red in bright daylight, meantime noting the visible changes which may occur. Exceedingly pure waters may show no change, or at most a slight browning, which rapidly disappears. In such a case the loss on ignition is usually small. Very impure waters containing much nitrate may show the same appearance, or there may in some cases be seen a momentary glow in some spots. The loss on ignition is then likely to be high. Frequently, however, the solids on ignition blacken, and burn white with some difficulty. If the water contains much organic matter of vegetable origin (peaty waters, etc.) this phenomenon may be very marked. The indications, however, only suffice to afford grounds for a surmise as to the quality of the water, which must be decided by further examination. After ignition, cool, allow to stand for a short time, and weigh. The loss is recorded as "*Organic and Volatile Matter (Loss on Ignition)*." The loss may be due partly or entirely to dehydration of certain salts (as calcium sulphate) or to partial dissociation of certain others (chlorides, alkaline carbonates, etc.), so that, except in connection with others, this test gives no positive information. The weight of the non-volatile residue—the difference between "Total Solids" and "Loss on Ignition"—is usually recorded as "Mineral Matter" "(Non-Volatile)." Some chemists moisten the solids after ignition with carbonic acid water or weak ammonium carbonate solution in order to restore carbonates, and then dry and weigh to get the loss on ignition. The English analysts as a rule do not record (in their reports) the amount of loss on ignition, because it is liable to be misunderstood or misinterpreted.

The residue after ignition should be treated with about 10 c. c. of water to which has been added a few crystals of ammonium nitrate and a few drops of nitric acid. This solution is then poured into a test-tube, and tested with a

little ammonium molybdate solution for the presence of phosphates. By making this test thus, upon the solids obtained from the same quantity of water every time, the proportion of phosphates may be roughly estimated, and may be recorded as "none," "faint trace," "trace," etc.

The amount of "Total Solids," etc., thus obtained, will also serve in a general way as a guide to the amounts which had best be taken for the determination of silica, lime, etc., for which the aim should be to work upon approximately 1 gramme of solids, unless that should require over 8 to 10 litres. For determining the amount of sulphuric acid in combination in the water, the best guide as to the amount to be taken will be a qualitative test on some of the unconcentrated water with barium chloride, after acidifying with hydrochloric acid. For the other tests the amounts here prescribed should be taken.

In this country it is customary to report analysis of water as made on 1 U. S. gallon of 231 cubic inches, containing a certain number of grains, which number has been fixed upon in the Columbia College School of Mines as 58,318. The weights and measures used are French. This involves a short calculation to convert milligrammes into the corresponding number of grains. One milligramme is one millionth of 1 litre. Suppose that upon evaporating 1 litre of water 1 milligramme of solid matter was left, the quantity will be one millionth of 1 litre. If a gallon of the same water were used, the solid matter would amount to one millionth of 1 gallon, or, as the gallon is assumed to contain 58,318 grains, one millionth of 58,318, and any number of milligrammes will correspond to that number of millionths of 58,318 grains. Therefore, the number of milligrammes multiplied by 58,318 and divided by 1,000,000 will give the number of grains in 1 U. S. gallon of 231 cubic inches. This rule applies to the calculation of all the constituents found by analysis. Then, to determine the number of grains of *organic and volatile matter* in 1 gallon of the water under examination, calculate the

number of milligrammes which would be lost by treating the residue left after evaporating 1 litre of the water as directed above, multiply this by 58,318, and divide by 1,000,000. The difference between the weight of dry residue before ignition and the sum of the constituents found by analysis, allowing for the loss of the water and part of the carbonic acid of acid carbonates, should not amount to more than a small fraction of a grain. If it does, the analysis should be repeated. This remark applies only to water containing a small amount of mineral matter. In the analysis of mineral waters, if it is desired to determine the "total solids" as a check on the correctness of the analysis, another method is pursued, which will be explained later.

Silica, Lime, Magnesia, Alumina, and Oxide of Iron.—To determine these, evaporate in a platinum dish nearly to dryness on a sand-bath (finishing the evaporation to dryness on a water-bath), from 2 to 8 litres of water, according to the purity of the water, having previously acidulated it with hydrochloric acid. Then dry the residue in an air-bath at 110° C., until the odor of hydrochloric acid cannot be detected, and proceed exactly as directed in the analysis of limestone. For this part of the analysis of Croton water, 5 litres will be sufficient. The evaporation may be made in porcelain instead of platinum, but there is danger of introducing a small amount of silica and alumina into the analysis. As in the analysis of water of this character it is unnecessary to separate the small amount of alumina and oxide of iron, they are generally weighed together, and reported as alumina and ferric oxide.

Sulphuric Acid.—Acidulate from 1 to 4 litres of the water with hydrochloric acid, evaporate to about 100 c. c., filter, if necessary, and determine SO_3 as in analysis of magnesium sulphate. For this determination in Croton water, 2 litres will be sufficient.

Chlorine.—For most potable waters it suffices to titrate directly with a hundredth or two-hundredth normal solution of silver nitrate (1.7 gms. or 0.85 gm. per litre). In most cases the proportion of chloride is so small, that comparison solutions must be used. Take two small white porcelain casseroles, and in each put 100 c. c. of the water. Add to each the same amount (5 to 6 drops) of potassium chromate solution (indicator). Both should now show the same tint. Placing these side by side, run into one of them, drop by drop from a burette, the standard silver nitrate solution until, as seen by comparison with the other solution, the tint becomes more red, the redness not being removable by vigorous stirring, and becoming also more marked on adding a few more drops of the silver nitrate. Note the reading of the burette at the point where the permanent change occurred; then add to the first solution a little solution of some alkaline chloride, stir in well and use this solution as a comparison solution for the titration of the contents of the second casserole, conducting the operation in the same manner as before. With this second casserole the conditions of bulk of solution, amount of suspended silver chloride, etc., are so nearly identical with the first when the titration is at the finishing point, that very accurate results may be obtained.

With waters containing much alkaline earth carbonate (temporary hardness), boiling to precipitate the carbonates may be necessary as a preliminary to the titration. If the alkalinity of the water is due to sodium carbonate, the addition of *very dilute* nitric acid in amount sufficient to exactly neutralize should precede. This may be determined by the aid of methyl orange *in the cold*, the acid being added from a burette.

Concentration of some measured amount of the water (as one or two litres) to a small bulk, previous to titration, and using a stronger solution of silver nitrate, is a plan preferred by some, when chlorides are small in amount,

but by proceeding as above described, the necessity for such elaboration may usually be avoided.

Sodium and Potassium.—Acidify 1 to 5 or 6 litres of the water with a few drops of hydrochloric acid, and evaporate to about 100 c. c., then render it alkaline by addition of saturated solution of barium hydrate, adding the latter until it fails to produce any further precipitate. Boil, filter, and wash all chlorides from the precipitate. Concentrate the filtrate if necessary, and separate the excess of barium by adding *in the cold* ammonia and ammonium carbonate solutions; let it stand for some little time, stirring occasionally until the precipitate becomes granular. Then filter, and wash with a dilute solution of the precipitant.

Evaporate the filtrate and washings in a platinum dish. As a small amount of magnesium may have escaped precipitation, ignite cautiously to expel ammonium salts, dissolve in water, filter, and treat the solution with a few c. c. of the barium hydrate solution, removing the excess of barium from the solution as before. It must be remembered that magnesium cannot be removed from a solution by the use of barium hydrate if any ammonium salts are present.

The filtrate from the second precipitation of barium carbonate should be heated in a weighed platinum dish until all odor of ammonia is gone, when it may be acidified with sulphuric acid in excess, evaporated to dryness, and ignited. A second ignition after sprinkling the residue with pulverized ammonium carbonate will be necessary to obtain neutral sodium and potassium sulphate.

At this point strong ignition will do no harm. Some prefer to weigh the alkalies as chlorides instead of as sulphates, but that method requires much greater care in igniting, and avoidance of a high heat, lest potassium chloride be lost by volatilization.

The mixed sulphates should give a clear solution with about ten times their weight of water, on warming gently.

If such is not the case, filter, evaporate and ignite, and weigh again. Then dissolve in a little water, add platinic chloride, evaporate, etc., determining potassium by the Lindo-Gladding method (see Potash Alum). Calculate the potassium so found to sulphate, and reckon the remainder of the mixed sulphates as sodium sulphate. Calculate both sodium and potassium according to the requirements of the case, as suggested in the section on grouping the constituents.

Hardness.—Waters are said to be “hard” to the extent to which they destroy soap and prevent it from making a lather. All waters, even distilled water, possess this property in some degree, the hardness increasing chiefly with the proportion of lime and magnesia which they contain (especially the former). Hence it has become customary to reckon “degrees of hardness” in their equivalent in calcium carbonate (CaCO_3). The Germans reckon in the equivalent of lime (CaO).

“Degrees of Hardness” usually means a soap-destroying power equivalent to so and so many grains of calcium carbonate per gallon (U. S. gallon 58,318 grains; English (Imperial) gallon 70,000 grains), though the term is used by some in the sense intended by the French, viz., parts of calcium carbonate in 100,000. The German degrees of hardness are given in parts of lime (CaO) per 100,000.

Two kinds of hardness are recognized — *Temporary*, which is destroyed by boiling; and *Permanent*, which is not removed by boiling. The sum of the two is called *Total Hardness*. “Hardness before boiling” is therefore the same as Total Hardness, while “Hardness after boiling” is “Permanent Hardness.”

Temporary Hardness is due to the alkaline earth carbonates held in solution in virtue of the carbonic acid in the water. On boiling the carbonic acid is expelled, and these carbonates precipitate.

Permanent Hardness is due chiefly to alkaline earth

salts (chlorides, sulphates, etc.), which are not dissociated by boiling.

The soap test, originally devised by Clark of England as a guide in his method of softening water, has been much used as a means for determining hardness, although it is open to numerous objections on the score of accuracy.

For the soap test, a "strong soap solution" containing 10 gms. of good white castile soap (with 12 per cent of water) in one litre of 90 per cent alcohol is first prepared. Of this solution 100 c. c. is mixed with 100 c. c. of water and 33 c. c. of strong alcohol, which affords the test solution.

This solution is standardized by dissolving 1 gm. of pure calc spar in hydrochloric acid, evaporating the solution with frequent addition of water until it is neutral, and then diluting to one litre. After mixing well, 1 c. c. = 0.001 gm. CaCO_3 . In a glass-stoppered bottle of about 200 c. c. capacity place 10 c. c. of the above solution (equivalent to 10 mgs. CaCO_3), add 90 to 100 c. c. of water, and then run in the soap solution from a burette, stoppering the bottle and shaking vigorously from time to time. When enough of the soap solution has been added to give a lather on the surface, which persists after standing quietly for five minutes, the titration is terminated. The amount of soap solution required is usually from 4.5 to 6 c. c. Whatever the amount, calculate the value of the soap solution in terms of calcium carbonate which constitutes the standard. The standard, however, is only true for exactly the same conditions, and varies with the temperature, with the amount of magnesium salts present, with the amount of alkaline salts present, and with the amount of alkaline earth salts present in the water (degrees of hardness), and possibly other conditions.

The errors due to excessive hardness of a water may to some extent be neutralized by diluting a known bulk of the water (5, 10, or 20 c. c., etc.) to 100 c. c., and then applying the test; but results by this test are at best only approximate, and in some cases not even that.

Hehner's alkalimetric method for determining hardness (*Analyst*, VIII., 77) is more rational, and affords results more in accord with the results by complete analysis.

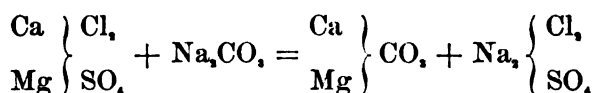
For this method prepare hundredth normal solutions of sulphuric acid and of sodium carbonate (0.98 gm. H_2SO_4 and 1.06 gms. Na_2CO_3 per litre respectively). 1 c. c. of either of these solutions is equivalent to 0.001 gm. CaCO_3 . They of course neutralize each other, c. c. for c. c.

As indicator, methyl orange is preferable on account of its indifference to carbonic acid.

For "temporary hardness," 100 c. c. of the water is placed in a small porcelain casserole, a few drops of methyl orange added, and the sulphuric acid run in from a burette until the indicator shows neutrality. It is preferable to conduct the test in duplicate, using the one as a comparison solution for the other, in the manner suggested regarding the titration for chlorides. The amount of sulphuric acid solution required in c. c. gives directly the parts per hundred thousand of temporary hardness.

For "permanent hardness" take another 100 c. c. of the water in a *platinum* dish, and add to it an excess of the sodium carbonate solution. In the absence of any other guide as to how much will constitute an excess, it will be safe to add as many c. c. of the sodium carbonate as there are *milligrammes* of "total solids" in 100 c. c. With many waters containing much salts, this may constitute an unnecessarily large excess. Then evaporate nearly or quite to dryness. Now fit a *small* paper in a funnel, and wash it three or four times with freshly boiled distilled water. Then wet down the contents of the dish with 5 to 8 c. c. of the same distilled water, rinse it about, and pour onto the paper, catching the solution in a small clean casserole. Rinse the dish a second and a third time in the same way, letting the filter empty itself each time, before pouring any more on. Add a few drops of methyl

orange to the solution in the casserole, and titrate with the sulphuric acid. The difference between the amounts of sodium carbonate and sulphuric acid solutions used gives permanent hardness in parts per hundred thousand. The *rationale* is easily made apparent: the difference spoken of represents the number of c. c. of sodium carbonate, the alkalinity of which was destroyed by reaction with the salts, affording permanent hardness to the water. By the evaporation the temporary hardness was destroyed by decomposition of the alkaline earth bicarbonates, and therefore had no effect by the time the titration occurred. With the salts causing permanent hardness the reaction was essentially



that is, each equivalent of calcium or magnesium (chloride or sulphate) afforded calcium or magnesium carbonate (which is filtered off) and sodium chloride or sulphate (which is neutral). The final titration therefore indicates only the amount of sodium carbonate added in excess.

Evaporation in platinum is necessary to avoid any errors which might be caused by the action of the sodium carbonate upon the silica of glass or porcelain. *Freshly boiled* distilled water is necessary to avoid taking up any alkaline earth carbonates on account of the presence of carbonic acid or ammonia. As little water as possible should be used in dissolving off from the dish for the same reason.

Permanganate Test.—To determine the amount of readily oxidizable organic matter in a water the permanganate test has been used. Various methods have been used, no two of which will afford the same or comparable results. The variations are as to the amount of permanganate used—whether barely sufficient or in excess, the length of time it is allowed to act, the temperature—whether at ordinary temperatures or at boiling heat, its

use on the water in its natural state or acidified, or rendered alkaline, etc.

Tidy's method (*Jour. Lond. Chem. Soc.*, XXXV., 67) is much used by English analysts. The permanganate solution used in this test contains 0.316 gm. $\text{K}_2\text{Mn}_2\text{O}_8$, per litre (1 c. c. = 0.00008 gm. O), or 0.395 gm. $\text{K}_2\text{Mn}_2\text{O}_8$, per litre (1 c. c. = 0.0001 gm. O).

Two or three lots of 250 c. c. each of the water are treated in stoppered flasks with 10 c. c. of the permanganate solution, and 10 c. c. of sulphuric acid (1 : 3 by volume). The sulphuric acid should be previously tested with permanganate, upon which it should exert no decolorizing effect at ordinary temperatures during at least four hours.

Blanks, or 250 c. c. lots of pure distilled water, charged with permanganate and sulphuric acid in flasks of the same shape and character, are also prepared.

All of the flasks are immersed in water, and kept uniformly at 80° Fahr. during the operation. If at any time while standing the color of the solutions becomes decidedly paler, 10 c. c. more of the permanganate solution must be added to maintain the presence of a decided excess. At the end of specified intervals the contents of the flasks are tested, to determine how much permanganate remains undestroyed. The intervals specified by Tidy are 2 minutes, 15 minutes, one hour, two hours, three hours, and four hours. This would require six flasks for each sample of water tested, besides the six blanks, each of which has to be examined at the same time with the test samples. The Society of Public Analysts of Great Britain recommend only using the fifteen-minute and the four-hour test (which latter usually shows nearly the same results as a three-hour test). At the end of the interval a few c. c. of a ten per cent solution of potassium iodide is added, and the iodine, set free by the permanganate hitherto undecomposed, is titrated by standard sodium thiosulphate (about 0.5 gm. per litre). The results with the blanks practically

affords a standard for the conditions under which the test was conducted, and the amount of oxygen absorbed may be calculated.

The Kubel-Tiemann method is used chiefly in Germany. For this a solution of permanganate of the same strength as above is prepared, also a solution of oxalic acid of corresponding strength, *i. e.*, that will decompose the permanganate c. c. for c. c. Then 200 c. c. of the water are placed in a flask, 10 c. c. of sulphuric acid (1 : 3 by volume) added, an excess of the permanganate solution is run in from a burette, and the water boiled for ten minutes, permanganate being added if necessary, so as to maintain an excess. Then remove the heat, add 10 c. c. of the oxalic acid solution, or more if that does not suffice to decolorize, and then run in permanganate until it imparts a permanent pink tinge. From the amounts of permanganate and oxalic acid solutions used, the amount of oxygen absorbed by the water may be calculated.

The indications afforded by the permanganate test, however applied, are easily capable of being misinterpreted. It is noticeable that, as a rule, organic matter of vegetable origin has the most decided effect on the permanganate, whereas that of animal origin, which is undoubtedly the more dangerous, affects it comparatively less. Hence many peaty waters, the sanitary purity of which is really high, may be made to seem very inferior by this test, and really dangerously polluted waters may seem to be of fair quality. On this account many analysts have abandoned the use of this test altogether.

Free and Albuminoid Ammonia.—This process, devised by Wanklyn, was first described in papers read before the London Chemical Society in 1867. The principles applied are, that on boiling dilute solutions containing nitrogenous organic matter with an alkaline solution of potassium permanganate an amount of ammonia is formed which bears a constant ratio to the proportion of nitrogenous organic substance present. Albumen yields about two thirds of

its nitrogen as ammonia, some classes of substances yield all, some one third, some one half, some one quarter, etc. Also, on distilling a solution containing free ammonia that compound comes over in the first portions, and may thus be concentrated sufficiently to make even small amounts determinable by the use of the Nessler reagent.

For the process one requires:

1. Strong solution of sodium carbonate. (The exact strength is unimportant.)

2. Alkaline potassium permanganate.—8 gms. of crystallized potassium permanganate with 200 gms. of caustic potash, or a corresponding amount of caustic soda, in one litre of water. The solution should always have the red-violet color of the permanganate. If it turns green either in the stock bottle or when in use in the retort, no trustworthy results can be obtained.

3. Nessler reagent.—35 gms. of potassium iodide are dissolved in about 800 c. c. of water, and the solution heated nearly to boiling. A cold saturated solution of mercuric chloride is then added little by little, especially towards the last, until the red precipitate of mercuric iodide just fails to redissolve even on stirring vigorously. Then 160 gms. of solid caustic potash or 120 gms. of solid caustic soda are dissolved in as little water as possible, and the solution poured into the mercury solution. The solutions should be *cold* when mixed. Let stand. After standing over night, 3 to 5 c. c. of saturated solution of mercuric chloride is added, the solution well stirred, and again allowed to settle. After settling a second time the clear solution should be fit for use. Its sensitiveness should be such that about 1.5 c. c. of the reagent, when stirred into 50 c. c. of water containing 0.005 mgm. of ammonia, will, in the course of 3 to 5 minutes, at ordinary temperatures, show a perceptible yellow tint. If this degree of sensitiveness has not been attained, add a little more mercuric chloride solution, stir in, let settle, and test again. The quality of the reagent seems to improve with

time. The depth of tint obtained with the Nessler reagent upon dilute solutions of ammonia depends upon the amounts of ammonia, the quality of the reagent used, the quantity used, the time it is allowed to act, and the temperature. If the amount of ammonia passes a certain proportion, a red precipitate and not a coloration is obtained. The presence of certain salts also affects the colorations produced with the Nessler, and it may also be noted that minute traces of hydrogen sulphide afford tints which closely simulate those obtained with ammonium salts.

4. Ammonia-free water. — This is best prepared by distilling a fairly pure water (distilled or other), and collecting the distillate. What comes over at first usually contains some ammonia, so that the distillate should not be put aside for use until it is found to run free from ammonia, as shown by the Nessler test. When the contents of the retort run low, ammonia will again make its appearance in the distillate. If a little sodium carbonate or other alkaline substance is added to the contents of the retort, the ammonia will be more quickly driven out than if such addition is not made. Another way of managing is to add a little sulphuric acid to the retort, and thus to hold back the ammonia from going into the distillate.

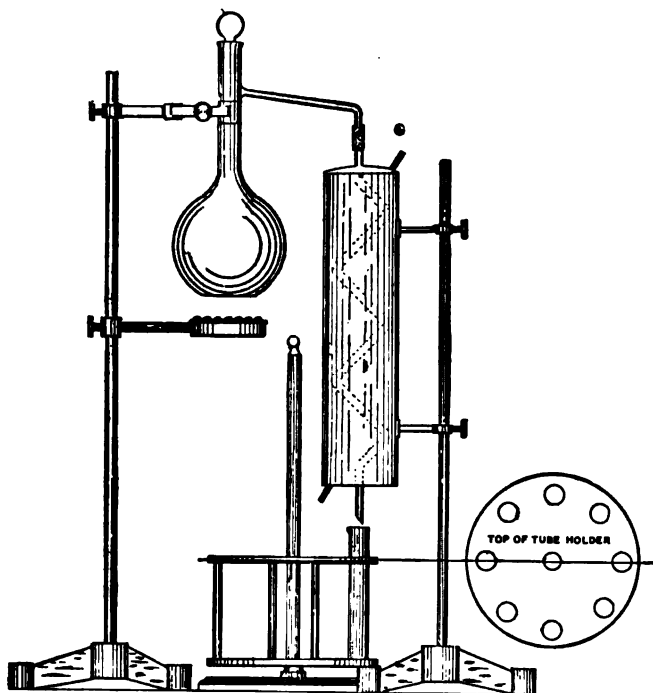
Methods of preparing ammonia-free distilled water by boiling off the ammonia in a large flask and using the remaining water, or expelling the ammonia by passing a current of steam through the water, do not give a satisfactory product, apparently because the hot distilled water acts upon the glass, and on testing with the Nessler a cloudy solution results.

On long standing in glass at ordinary temperatures the same result will often be noticed.

The ammonia-free water should be kept in glass-stoppered bottles provided with caps to protect the lips from deposition of ammonia compounds from the air of the laboratory.

5. Standard ammonia solution.—For a stock solution dissolve 0.315 gm. of ammonium chloride, or 0.3883 gm. of ammonium sulphate in water, and dilute to one litre, using ammonia-free water. Of either solution 1 c. c. = 0.1 mg NH_3 . For making up the standards for comparison dilute 10 c. c. of the stock solution to 100 c. c., of which 1 c. c. = 0.01 mg NH_3 . At present Wanklyn recommends to make the stock solution ten times as strong as the above, and to dilute 1 c. c. to 100 for use.

Apparatus.—A very convenient form of apparatus consists in a two-litre flask with a side neck tube, the tube



being bent so as to point vertically downward at a convenient distance from the flask. A copper condenser carrying a block-tin zigzag is attached. (A zigzag gives a more steady drip of the distillate than does a helical

“worm.”) The delivery end of the tin tube is cut aslant. The lower end of the copper condenser is arched upward so that in case the condenser “sweats” the external condensed moisture will not drip into the receivers. A rotating stand, capable of accommodating eight receiving tubes (Nessler tubes) is also a great convenience. The tubes are not readily upset, and their relative positions are easily kept without special attention.

For the flask or retort a glass stopper is decidedly to be preferred. Rubber stoppers cannot be used at all, and in general, contact of the steam with rubber must be avoided, as the rubber will hold back ammonia. On this account, in making connection between the flask (or retort) and condenser, the connection between the two should be made as close as possible, and only a small piece of rubber tube used to hold the two together. In the arrangement sketched the glass tube should project three or four inches down into the tin tube, and a short piece of rubber tube be used to hold it in place, the glass tube fitting the tin tube rather closely. Similarly, if an ordinary tubulated retort with straight Liebig condenser is used the neck of the retort must be thrust into the condenser tube as far as it will go, and a short piece of rubber tube used to steady it in position. If one tube cannot be inserted within the other, cut the ends square, bring them together so that they abut closely, and cover the joint with a rubber tube.

The Nessler tubes should be of the same calibre, and made of the same kind of glass. The kind made with thickened bottoms, which have been ground off and polished down, are the best.

Inasmuch as the breaking of a Nessler tube is not an unusual occurrence, it will be found most convenient to purchase at one time a supply of between 30 and 50 tubes. Then in case of breakage one has a supply which correspond in calibre and in color of glass. Points in which it may be found exceedingly difficult to match one's set

when breakages have reduced the number to the point where for lack of Nessler tubes it may become troublesome or impossible to conduct a test. Some analysts prefer tubes having a capacity of only a little over 50 c. c., marked at 50 c. c. Others prefer tubes graduated to 50 c. c. and 100 c. c. with a capacity of a little over 100 c. c. The calibre of the tubes should be so nearly the same that the 50 c. c. lines on all should be within one sixteenth of an inch of one another.

The comparison rack for the Nessler tubes had best be of wood, painted black, with places for 10 or 12 tubes in one line. The tubes should stand on a sheet of plain glass raised high enough to allow the placing of a sheet of white paper beneath, as a background. It may rest on cleats at the sides. The advantage of having so many holes in the comparison rack is that the standards may be placed in every other hole, leaving the vacant spaces for the tubes to be compared. The operation is thus much facilitated.

It is well to mark the tubes used for standards by etching or by attaching gum labels, that they may not be confused with the tubes for testing distillates.

A bulb-stirrer—a tube with a bulb blown on one end—will be a necessary adjunct, besides pipettes, measuring flasks, etc.

Process.—It is best to have two retorts, one for “Free,” the other for “Total” ammonia. Put 300 to 400 c. c. of distilled water, or some fairly good potable water, in each. Add to the “Free” retort 5 to 10 c. c. of the sodium carbonate solution and to the “Total” 50 c. c. of the alkaline permanganate solution. Add also to each a couple of pieces of *ignited* pumice-stone, each about the size of a small pea. Boil both until 50 c. c. of the distillates show no color with the Nessler reagent. Meantime clean up 12 or 15 of the Nessler tubes by rinsing them thoroughly with water from the tap (if that is sufficiently free from ammonia to refuse to respond to the Nessler test).

By this distillation the retorts, connections, and reagents are thoroughly cleansed.

The water from a distillation should not come in contact with the outside of any of the apparatus or with the hands, as that would be sufficient to give ammonia by the Nessler test. Wiping out the tubes or other apparatus with filter-paper, or with a towel, no matter how clean, is inadmissible for the same reason.

The drip-tube of the condenser should not touch the Nessler tubes into which it delivers.

When the retorts are clean, shut off the heat, and to each retort add 500 c. c. of the water to be tested. The flask in which this is measured, and the funnel through which it is poured, should be well rinsed with the water to be tested before charging the retort. Then apply the heat again, and distill, catching the distillate in lots of 50 c. c. each. The rate of distillation should be 50 c. c. in 10 to 15 minutes. The number of fractions to be taken off varies with different waters; as a rough guide it is usually safe to take 5 from the "Free" and 7 from the "Total." Leave the retorts still distilling until it has been proven that all of the ammonia has distilled over.

While the distillation is in progress, dilute some of the standard ammonia solution so that a solution containing 0.01 mg. NH_3 per c. c. is obtained, and by means of a burette prepare a set of standard tubes containing respectively 0.01, 0.02, 0.03, and 0.04 mg. NH_3 . Tubes containing 0.005 and 0.05 mg. NH_3 may also be convenient in some cases. Fill all these tubes to the 50 c. c. mark with ammonia-free distilled water, pouring the water in so as to wash down the sides of the tubes.

When the standards are ready, and a sufficient number of tubes containing the distillate have been obtained (usually five for "Free" and seven for "Total") add to each tube of distillates and standards the same amount of Nessler reagent (about 1.5 c. c.) in as rapid succession as possible, adding to the weakest first. The absolute

amount of Nessler added to each, whether 1.25, 1.5, or 2 c. c., is unimportant, the only point requiring attention being that the *same amount* of Nessler goes to each.

Then, by means of the bulb stirrer, mix the contents of each tube by moving the stirrer up and down, taking care not to strike it against the bottom. Let the tubes stand for five minutes, and then compare the distillates one by one with the standards. The comparisons are made by *looking down* through the tubes. Differences of less than 0.01 mg NH₃ are estimated and the results recorded. Always *reverse* the relative positions of the tubes compared before deciding upon the reading, since the left-hand tube usually appears the darker when both are the same.

If any of the distillates show a stronger color than that given by the 0.04 (or perhaps 0.05) tube, dilute to 100 c.c. with ammonia-free water, mix well by pouring back and forth into a clean tube or beaker, pour off 50 c.c., add half the amount of Nessler solution, let stand and compare again, noting the fact of such subdivision.

When adding the Nessler, if the policy of adding to the weakest first is pursued, one often receives warning before adding to the first or strongest distillates, that they are likely to show too high a color, and dilution may be made in the manner described before adding the Nessler.

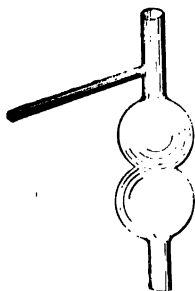
By keeping note of the order of the distillates the rate of evolution of the ammonia can be observed. Vegetable organic matter gives up albuminoid (*sc.* total) ammonia more slowly than does animal organic matter.

To get albuminoid ammonia deduct the amount of "Free" from that of "Total."

Total Nitrogen (Kjeldahl process). The description here given is essentially that published by Drown and Martin (*Jour. Analyt. and App. Chem.*, III., 258, 1889) with some few modifications which have been found convenient in practice.

Apparatus: Besides condensers, measuring-flasks, pi-

pettes, etc., it is necessary to have on hand four or five Bohemian-glass flasks, with *round bottoms*, quart size, the sizes of the necks being fairly uniform, so that all can be fitted with the same cork. Also two or three Wurz tubes, the upright tubes of which should have about half an inch internal diameter both above and below the bulbs. The constriction between the bulbs should not be less than half an inch in the clear.



Fit the delivery tube of a Wurz tube to a condenser, connecting it in such a manner that the steam shall come in contact as little as possible with the rubber tube which steadies the connection, as suggested regarding the "Free" and "Total" distillation.

On the lower end fit a cork which is adapted to the flasks, so that any one of them can be attached for purpose of distilling.

Reagents: The ordinary reagents for the Wanklyn method must be provided: Nessler, standard ammonia solution, etc. Rather more ammonia-free water is needed for each than in the case of the Wanklyn method. It is also necessary to set apart a bottle of concentrated sulphuric acid for use in this process, the contents of which in ammonia must be determined in a manner hereafter to be described. One also requires a solution of potassium or sodium hydrate containing in the proportion of about 200 gms. of the sticks per litre. After dissolving in this proportion, add potassium permanganate (about 2 gms. per litre) and boil for some little time, say reducing the bulk by about one fifth. The boiling is most easily managed if one adds a few fragments of ignited pumice. This solution should always be boiled for a short time before using, to avoid introducing ammonia from this source. The reason is that stick potash or soda is purified by fusion with a little nitrate, and enough nitrogen com-

pounds always remain to give ammonia perceptible by the Nessler test on standing in solution containing permanganate.

Process.—Cleanse the condenser and connections by attaching one of the flasks containing about 300 c. c. of water and a little sodium carbonate, also a fragment of ignited pumice, and distill through the condenser about 100 c. c. of water. Then cleanse thoroughly another of the flasks, rinsing it finally with ammonia-free water, and place in it 500 c. c. of the water to be tested, also a fragment of freshly ignited pumice. When the condenser, etc., has been cleaned, attach this flask, and distil for free ammonia, catching the distillate in 50 c. c. lots, which are Nesslerized as usual. Four tubes (200 c. c.) will usually contain all the free ammonia. Then detach the flask, after cooling somewhat, and add 10 c. c. of the concentrated sulphuric acid. The acid should not be poured from the bottle, but should be taken out with a pipette, which must not be allowed to touch the sides of the neck. One pipette-full should be drawn out and thrown away, before drawing a pipette-full for addition to the water.

Then place the flask on a wire-gauze support on a ring-stand in a slanting position, the wire-gauze being bagged down so as to partially embrace the curvature of the flask, as usual in Kjeldahl determinations.

Put a burner under the flask, and boil down to sulphuric acid fumes, and continue the heating until the acid becomes colorless. The use of mercury, or addition of potassium permanganate at the end, is unnecessary. Then cool, and dilute with about 200 c. c. of ammonia-free distilled water. Then add about 100 c. c. of the solution of caustic alkali to which reference has already been made, attach to the condenser again, and distill off about 150 c. c. which is diluted to 200 c. c., well mixed, and 50 c. c. taken for the Nessler test. An additional 50 c. c. had best be distilled off, and tested with the

Nessler to make sure that no more ammonia is obtainable from the flask.

The result on 50 c. c. multiplied by 4 gives the ammonia due to organic nitrogen, obtainable from 500 c. c. of the water, plus that due to the sulphuric acid, which must be deducted. To obtain the correction for the sulphuric acid, it will be found practically impossible to obtain water absolutely free from organic nitrogen. It is therefore necessary to carry through the test with a fairly pure (preferably distilled) water, using 5 c. c., 10 c. c., and 20 c. c. of the concentrated sulphuric acid, and from the results so obtained the ammonia due to 10 c. c. of the acid may be estimated, assuming of course that the ammonia obtained from the water is the same in every case.

Exposure of the water when acidified to the atmosphere of the laboratory must be avoided as much as possible.

The plan of acidifying the original water and boiling down directly, and afterwards deducting the free ammonia, although it has some advantages, does not seem so satisfactory as the plan here sketched out.

Drown and Martin find that in general terms the organic nitrogen as ammonia is about half the albuminoid ammonia in *natural* waters. My own results tend to confirm this statement.

Nitrates.—Of the numerous processes for the estimation of nitrates, two may be here mentioned—the zinc-copper couple, and the phenol-sulphuric test.

For the zinc-copper couple test, nearly fill a wide-mouthed, glass-stoppered bottle, holding 300 to 400 c. c., with zinc turnings cut in curls so that they occupy much space with large interstices. Cover the zinc with water, and pour upon it a dilute solution of copper sulphate. Allow it to stand until the zinc has become entirely coated with a black, strongly adherent coating of copper. If the copper solution is too strong, the coating will not adhere satisfactorily. Then wash the zinc three or four times with clean water, and finally wash it at least three times

with the water to be tested; wash the stopper at the same time. By a little care the zinc curls can be so lodged in the bottle that they will not fall out when the bottle is inverted. Then cover the zinc with the water to be tested, add about 0.200 gm. of pure oxalic acid crystals, insert the stopper, and stand it aside over night. Under the conditions produced the zinc slowly dissolves, hydrogen being evolved, which reduces the nitrogen of the nitrates first to nitrites, and eventually to ammonia. The next morning test some of the water in the bottle for nitrite by the naphthylamine test, hereafter to be described. If no nitrite is present the reduction is complete, and the test for ammonia may be made. If nitrite is present, the solution must stand longer to complete the reduction. A side test must then be made to determine what quantity of water must be used to bring it within the limit of 0.04 or 0.05 mg. ammonia, and according to the indications take a measured quantity of the water (5, 10, 20, or 25 c. c.), dilute to 50 c. c. with ammonia-free water, make up a set of standards, and Nesslerize as in the case of "Free" and "Total" ammonia. Of course it may happen that a full 50 c. c. of the water can be used for the test. From the reading, and the amount of water taken, calculate the amount of ammonia per litre. From this deduct the free ammonia, found elsewhere, and calculate the remainder to nitrogen, which is reported as "nitrogen in nitrates and nitrites."

The "picric acid," "phenol sulphonic," or Grandval-Lajoux process (*Chemical News*, LII., 42) depends upon the conversion of carbolic acid (phenol) into picric acid or analogous nitro compounds, by the nitric acid in the water, over-neutralizing with ammonia, which develops a strong yellow color for the amount of picrate present, and then determining the amount by colorimetric comparisons.

Make up, first, a standard solution containing 0.722 gm. pure potassium nitrate (= 0.100 gm. N) in one litre. This may be kept on hand. To make a test, dilute 10 c. c. of

this solution with 90 c. c. of water, making a solution one tenth this strength (1 c. c. = 0.001 mg. N ; 10 c. c. = 0.01 mg. N). Of this last solution take 10 c. c. and evaporate in a small porcelain capsule on the water-bath. Side by side with it evaporate 10 c. c. of the water to be tested in a corresponding capsule. Continue the evaporation to apparent dryness. Long heating is to be avoided. Some nitrite is introduced by long heating over a gas flame, while the effect of the heat alone is to diminish the quantity of nitrate.

Meantime make a mixture of phenol and concentrated sulphuric acid. 6 drops of the first with 30 of the last may be used. The proportions recommended by Grandval and Lajoux are 6 gms. phenol, with 37 c. c. of concentrated sulphuric acid and 3 c. c. of water. It has been found, however, that the results are inaccurate and unsatisfactory (as to quality of tint) if the reagent is not freshly prepared each time for use. Add 6 to 10 drops of the mixture to each dish, making sure to add the same quantity to each. Then by means of glass rods spread the solution about, so that it wets every part of the residue. Add about 1 c. c. of concentrated sulphuric acid to each, warm on the water-bath for two or three minutes, take off, cool, and dilute with water. Then add 5 c. c. of strong ammonia to each, when the color will develop. Rinse the solution from the water into a Nessler tube, and dilute to 50 c. c. The solution from the standard may be diluted according to requirements. For many waters it will be sufficient to dilute it to 100 c. c. and from this to take out lots of 10 c. c., 20 c. c., 30 c. c., and 40 c. c., each of which is diluted to 50 c. c. to afford a color scale. After matching the tint of the solution from the water, calculate up to the amount of nitrogen in nitrates to the hundred thousand, the gallon, or whatever unit may be adopted. If the water contains much chlorides, it is asserted that the results are inaccurate, which is probably true in extreme cases. Some claim that so long as the

phenol-sulphonic reagent is used fresh the chlorides will not interfere.

Of course the distilled water and sulphuric acid used must be free from any traces of nitric acid or nitrate.

Nitrites.—The most delicate and satisfactory test for nitrous acid is the red coloration produced in acid solution by addition of sulphanilic acid and a salt of naphthylamine (Griess, *Berichte*, XII., 427). The presence of acetic acid makes the reaction occur more promptly. Warming also hastens it. The tint, which very much resembles that of weak potassium permanganate solutions, is said to be perceptible when the water contains but one part of nitrous acid in one thousand million.

Ilosvay's method of preparing the reagents is to be recommended.

Sulphanilic acid: Dissolve 0.5 gm. in 150 c. c. of acetic acid (of sp. gr. 1.04; about 30 per cent).

Naphthylamine acetate: Boil 0.1 gm. solid naphthylamine in about 20 c. c. of water, filter off, and to the clear solution add 180 c. c. of dilute acetic acid.

Keep these solutions separate, and mix 2 c. c. of each just before making a test. If a color develops on mixing them, pass the solution through bone-black, or add a few drops of sulphuric acid and one or two small pieces of zinc, and allow the mixture to stand until it becomes colorless.

Then acidify the water to be tested with a few drops of sulphuric acid, and add 5 c. c. of the mixed reagent, stir, and allow it to stand for some time. The color develops fully in less than 20 minutes at ordinary temperatures, or more rapidly if it is warmed. Placing the solution over a flame, however, involves the risk of introducing nitrite from the products of the combustion. In such cases, however, if the liquid has been undisturbed a coloration due to causes of this kind will be observed only in the upper layers of the solution.

If a quantitative estimation is desired, measured amounts

of the water (50 c. c. or 100 c. c.) must be used, and a standard solution for colorimetric comparison is also needed. The potassium or sodium nitrite supplied for laboratory use is not pure enough for this purpose. Silver nitrite (AgNO_2) must be prepared. Mix together strong solutions of potassium (or sodium) nitrite and of silver nitrate, filter immediately, and allow the clear solution to cool. The silver nitrite formed is quite soluble in boiling water, but crystallizes out on cooling. Collect the crystals, redissolve in a limited amount of boiling water, filter, and recrystallize. Drain off the mother liquor, dry on the water-bath, and then in a desiccator. 11 gms. of this salt contain 1 gm. of nitrogen. The salt should not be exposed to a strong light during or after preparation.

Weigh out 0.275 gm. of the dry salt, dissolve in a little hot water, add a slight excess of sodium or potassium chloride, filter off the silver chloride, and wash, bringing the filtrate and washings up to a bulk of 250 c. c. Mix well. For making comparison standards dilute 10 c. c. of this solution (= 0.001 gm. N) to one litre. After mixing well, make up standard solutions containing 1 c. c., 2 c. c., 3 c. c., etc., of this dilution. The use of 100 c. c. each of standard solutions and of the water tested is preferable. Add the same amount of the reagent to each. Mix; let stand (covered) 20 minutes, and then compare.

Appearance is usually ascertained by looking through two feet of the water in a tube of colorless glass, toward a sheet of white paper. A tube of about an inch in diameter, constructed like a long Nessler tube, is a convenient form for the purpose. The color, and presence or absence of turbidity are the points to be noted.

Odor.—To a clean flask of about one litre capacity fit a cork carrying a thermometer, the bulb of which extends down into the body of the flask. Introduce 400 or 500 c. c. of the water, cork up and then warm the water up to 100° Fahr. (38° C.) as indicated by the thermometer. Shake well, uncork, and immediately try the odor.

Grouping the Constituents Found by Analysis.—It is almost impossible to give rules for grouping the constituents so as to meet all cases. It will be sufficient to give directions for grouping the results of analysis of such water as is at all likely to be used for drinking or manufacturing. Combine the sodium with chlorine as sodium chloride, and the potassium with sulphuric acid as potassium sulphate. Should there be any more sodium than the chlorine will satisfy, and more sulphuric acid than is required by the potassium, combine the excess of sodium with sulphuric acid as sodium sulphate, and should there be more sodium than the sulphuric acid will satisfy, calculate the excess to sodium carbonate. Should there be more than enough sulphuric acid to combine with sodium and potassium, combine the excess first with calcium, as calcium sulphate, and any further excess with magnesium as magnesium sulphate. If the water contains a large amount of chlorine (more than enough to satisfy the sodium), and not enough sulphuric acid to satisfy the potassium, combine the excess of potassium with chlorine, and if there be any chlorine still left, combine it first with magnesium, and then, if there be more than enough to saturate the magnesium, combine the excess with calcium. Calculate all calcium and magnesium not combined with chlorine and sulphuric acid to carbonates.

This method of grouping the constituents in most cases very nearly represents the facts so far as can be ascertained for potable waters. With very saline waters, containing little or no alkaline carbonate and much chloride, it probably does not. In such cases some analysts evaporate one litre or more to dryness, and then treat the solids with strong alcohol, filter off, examine the two portions separately, and calculate the groupings from the data thus afforded.

The following table may be found of use in the analysis of mineral and potable waters for the calculation of the number of grains in the U. S. gallon of 231 cubic inches,

the number of milligrammes per litre having been found. The number of grains in the gallon has been taken as 58,318, which is believed to be the most correct figure, though authorities on the subject differ slightly from one another, *e. g.*, the U. S. Dispensatory gives 58,328.886, or nearly 11 grains more. Either of these results gives about 133.3 avoirdupois ounces in the gallon.

Table showing the number of grains in the U. S. gallon of 231 cubic inches, corresponding to the number of milligrammes in one litre, by E. Waller, A. M., E. M.

MGS. TO 1 LITRE = GRS. TO U. S. GAL.	MGS. TO 1 LITRE = GRS. TO U. S. GAL.	MGS. TO 1 LITRE = GRS. TO U. S. GAL.	MGS. TO 1 LITRE = GRS. TO U. S. GAL.
1...0.058818	26...1.516268	51...2.974218	76...4.482168
2...0.116636	27...1.574596	52...3.032536	77...4.490486
3...0.174954	28...1.632904	53...3.090854	78...4.548804
4...0.233272	29...1.691222	54...3.149172	79...4.607122
5...0.291590	30...1.749540	55...3.207490	80...4.665440
6...0.349909	31...1.807858	56...3.265808	81...4.723758
7...0.408226	32...1.866176	57...3.324126	82...4.782076
8...0.466544	33...1.924494	58...3.382444	83...4.840394
9...0.524862	34...1.982812	59...3.440762	84...4.898712
10...0.583180	35...2.041130	60...3.499080	85...4.957030
11...0.641498	36...2.099448	61...3.557398	86...5.015348
12...0.699816	37...2.157766	62...3.615716	87...5.073666
13...0.758134	38...2.216084	63...3.674034	88...5.131984
14...0.816452	39...2.274502	64...3.732352	89...5.190302
15...0.874770	40...2.332720	65...3.790670	90...5.248620
16...0.933088	41...2.391038	66...3.848988	91...5.306938
17...0.991406	42...2.449356	67...3.907306	92...5.365256
18...1.049724	43...2.507674	68...3.965624	93...5.423574
19...1.108042	44...2.565992	69...4.023942	94...5.481892
20...1.166360	45...2.624310	70...4.082260	95...5.540210
21...1.224678	46...2.682628	71...4.140578	96...5.598528
22...1.282996	47...2.740946	72...4.198896	97...5.656846
23...1.341314	48...2.799264	73...4.257214	98...5.715164
24...1.399632	49...2.857582	74...4.315532	99...5.773482
25...1.457950	50...2.915900	75...4.373850	100...5.831800

Deciding upon the *sanitary quality* of a water, is chiefly a matter of experience. Many points must be taken into consideration, such as the character of the supply (shallow well, artesian well, pond, river, etc.), the location, the geological formation, the season, etc.

The results of the tests must also be considered together, and the observations as to any one of them judged with reference to the others. In general terms, no hard and fast

"limits" can be adopted. Conclusions on any such lines would in many cases be erroneous, and moreover one would lay himself open to the accusation of absurdly regarding a certain number of germs (say six) harmless, and one or two more (say seven or eight) as dangerous.

To consider the tests seriatim:

Appearance has been claimed by some to be merely a matter of sentiment. However, in general terms the nearer the appearance approaches to that of pure distilled water, the greater the presumption in favor of its purity. A water which becomes opalescent on standing corked up for some hours is open to suspicion.

Odor.—Treatment in the manner described will often bring out a characteristic odor, indicating more or less positively the probable source of the water, or probable contamination. Absence of any characteristic odor is not, however, absolute proof of absence of contamination.

Water supplies, especially public ones, are often subject to the appearance of odors in them, due to the presence of certain algæ, which impart a very unpleasant smell, and sometimes taste, but which nevertheless may not materially affect the wholesomeness of the water.

Chlorine.—Sewage contains much chlorides, and even a small increase in that constituent may accompany an infiltration of considerable amounts of sewage.

Except in the vicinity of the ocean, the chlorine in chlorides is usually less than 1 per hundred thousand.

Near the ocean it may approach or even pass that amount. In certain geological horizons (notably in some of the beds of the Salina formation) a large amount of chlorides may be found in uncontaminated waters.

Local standards, drawn from such data as may be available, have to be established as to the normal amount of chlorine to be found in the uncontaminated waters of a district. The 1890 report of the Massachusetts State Board of Health gives a map of the state, showing the normal chlorine in different localities. The amounts vary

form 0.06 in the extreme northwestern corner of the state to 2.39 parts (per hundred thousand) at Provincetown, Cape Cod.

Any material departure from the normal constitutes grounds for suspicion. The season, also the occurrence of rains or else of drought at the time of taking the sample, have some influence, and must also be considered.

Phosphates.—Ordinarily, only minute traces can exist in potable waters, such waters being practically always alkaline from the presence of dissolved calcium and magnesium carbonates. In some cases the rocks or soil of the district naturally contain phosphates traces of which are to be found in the waters. Some waters when grossly contaminated, will contain in solution comparatively large amounts. The presence of traces of phosphates is therefore not always a suspicious sign, but must be considered in the light of what is known regarding the locality, and in relation to the results of other tests.

Nitrites.—It is asserted by some that the presence of nitrites is always a bad indication. This is not always true. Nitrites in small amounts are sometimes found in streams running through heavily wooded districts, which have extracted so much vegetable matter from the dead leaves, fallen trees, etc., that they are brownish ("weak tea") in color. Nitrites also may be found in some cases where the sample has been taken after heavy thunder showers, or electrical disturbances of the atmosphere. Whenever found, the indications afforded by the other tests should be very critically examined, to determine whether the unfavorable sign is sustained by other evidence.

Nitrogen in Nitrates.—In ponds and streams, etc., the amount is usually but 0.01 or 0.02 (per hundred thousand) especially when the season favors the growth of vegetable life. In wells, where the conditions are different, there is frequently ten times as much (0.1 to 0.2). The deeper the well, the more the opportunity for percolation through

soil containing the nitrifying ferment. Sewage, which has undergone no percolation contains little or no nitrates. Naturally, the proportion is higher in winter than in summer.

Waters containing 0.5 part or over, even though the "albuminoid ammonia" may be low, have been known to produce disease, and such should be regarded with suspicion. It has been asserted that when the nitrogen has passed into the form of nitrate, all danger is past. Experience, however, has not confirmed this view.

Free Ammonia.—This is usually low (0.001 to 0.003 per hundred thousand) in ponds and streams, etc., but sometimes much higher in the water from wells. About 0.01 or more is too large an amount even in wells to be passed without question, except in the case of artesian wells. Half that amount is high for ponds, etc.

"Free Ammonia" is sometimes called 'ureal' ammonia because urea in presence of other organic matter affords considerable amounts on boiling with sodium carbonate, and a high figure in some cases may be due to that cause.

Albuminoid Ammonia.—Wanklyn has put the limit for this constituent at 0.008 or 0.010 in fairly pure waters. With respect to well waters this limit might be accepted if the results of the other tests afford confirmatory evidence.

In the case of ponds, streams, etc., where dead leaves or other vegetable debris may get into the water, twice those amounts (0.016 to 0.020) may occur without being regarded as indicative of dangerous impurity. The rate at which the albuminoid ammonia distils over is of some importance. That of vegetable origin comes over more slowly than that of animal origin. The mode of conducting the distillation (distilling quickly or slowly, allowing the contents of the retort to become concentrated or not, etc.) has an influence on the figures obtainable, so that a uniform method of procedure is necessary to obtain comparable results.

Hardness.—Aside from the question of contamination, the sanitary value of hard waters has been much discussed, but no definite conclusions have been reached, except that for comfort and cleanliness soft waters are to be preferred, other things being equal.

Sewage water is quite hard, the hardness being almost entirely "permanent." An increase in the hardness of a water over the amount normal to any given district may be due to infiltration of sewage. More significance is to be attached to the ratio of "Total hardness" to "Total solids." This affords a rough gauge of proportion of alkaline salts present.

In uncontaminated waters the hardness may be three fourths or one half of the "Total Solids." If it is one third or a still smaller proportion of the "total solids," there is some reason for suspicion, which, however, needs to be confirmed by the other results. On the other hand sewage may be present in a water without affording any decided indication of this sort.

Organic and Volatile Matter. (Loss on Ignition.)—The behavior of the solids on heating to ignition is usually of more importance than the actual amount lost. Vegetable organic matter will blacken and then burn off with some difficulty—much more so than when the organic matter is of animal origin. When much nitrate is present there may be scarcely any perceptible blackening, and there may perhaps be seen a momentary glow here and there, resulting from the mutual destruction of the nitrates and organic matter, at the temperature used. In those cases the loss will be comparatively large. A high figure may also result from loss of water of crystallization from certain salts (calcium sulphate, etc.), or from partial dissociation of alkaline earth chlorides, etc. If the water contains deliquescent salts, the loss may also be high. The odor on burning off may also be of assistance in drawing conclusions.

One's clients (physicians and others) often attribute to

the figures for "Organic and Volatile Matter" a significance which they do not really merit, and partly on that account, partly on others, some chemists (notably in England) omit to report any figures for the same in their certificates.

Total Solids.—The amount will vary with the locality and conditions to which the water has been subjected. The season makes a material difference. In the northern United States the melting snows and frequent rains of the spring-time dilute the waters so that in April or May the solids are usually the lowest for the year. The highest figures are generally found in November or December. Infiltration of sewage tends to increase the proportion of solids.

The maximum amount of "Total Solids" regarded as admissible in uncontaminated waters for domestic uses has been put at about 50 parts (per hundred thousand).

NOTE.—In *examining ice* the samples should not be freely exposed to the air while melting, but should be enclosed in large wide-mouthed jars provided with stoppers. Two-gallon jars with mouths about five inches in diameter is a suitable size. After cleaning a jar thoroughly, introduce the ice in pieces as large as possible, avoiding, so far as may be, touching them with the hands. A small pair of fire tongs, well cleaned, is convenient for the purpose. Insert the stopper and allow the ice to melt about one fifth at the ordinary temperature of the room. Pour off the water, which has thus served to wash the ice, stopper again, and allow the remainder to melt, and thus afford a sample for testing.

The limits of purity for ice are naturally much lower than for the water from which it has been derived. Free ammonia may perhaps be as high as in the water, but all other constituents should be present in exceedingly small amounts (practically insignificant). Albuminoid ammonia should be less than 0.005 (per hundred thousand).

CHAPTER XXXIII.

MINERAL WATER.

The term "mineral water" is usually applied to water assumed to possess medicinal properties or containing an unusual amount of mineral matter. Such waters have been more or less elaborately classified, with respect to their therapeutic effects, but for analytical purposes it will suffice to classify them as non-sulphuretted and sulphuretted waters. The non-sulphuretted waters might be subdivided into alkaline and acid waters. The former comprise the larger proportion of the mineral waters with which the analyst has to deal, and the description of the methods is more particularly applicable to those of that class, of which the Saratoga waters may be taken as a type.

Total Solids.—Evaporate 100 c. c. of the water in a weighed platinum dish, dry thoroughly in an air-bath at 130° C., and weigh. The presence of various hygroscopic salts renders it extremely difficult to obtain a constant weight, or absolutely concordant results on different trials, but the results have an important value as a "control" test. Fresenius recommends also that this residue be treated with sulphuric acid, evaporated, ignited, and weighed, which gives the bases as sulphates, plus iron as ferric oxide, silica, and phosphoric acid (HPO_3), and thus gives a still closer check on the results.

Total Alkalinity.—Add a few drops of methyl orange to 100 to 500 c. c. of the water, and titrate with tenth normal acid. The result shows the alkalinity due to alkali and alkali earth carbonates. This test should be made upon the water when as fresh as possible, before it has had time to deposit alkali earth carbonates by loss of carbonic acid. The bases in the borates and silicates

present are in this titration reckoned in with those of the carbonates. The results are seldom reported, being used as a "control" test only. The acidity of acid waters may be determined in the same manner, *mutatis mutandis*.

Sodium Carbonate or Bicarbonate.—Treat 1 litre of the water essentially in the manner described in the previous chapter for permanent hardness by Hehner's method, omitting the addition of sodium carbonate solution, and using stronger alkalimetric solutions, *i. e.* evaporate in platinum or silver to dryness, treat the solids with several successive lots of hot, freshly boiled water, running each lot of water (5 to 10 c. c.) separately through the filter. When five or six washings have been performed, titrate the filtrate (cold) with tenth normal acid, using methyl orange as indicator. Wash at least once more, and note whether the alkalinity of the washings will require more than a drop or two of standard acid. If it does, wash some more in the same manner. The c. c. of tenth normal acid required to neutralize multiplied by 0.0084 will give the amount of NaHCO_3 present, to which form it is usually reckoned. In some cases some MgCO_3 will dissolve, and thus afford results higher than the truth.

Silica, Ferric Oxide, Alumina, Lime, and Magnesia.—Acidulate 1 litre, or enough to afford 1 gramme or over of salts with hydrochloric acid, evaporate to dryness, take up with hydrochloric acid, and proceed as in the analysis of limestone.

In the case of certain (acid and alum) waters, the iron and other members of the ammonium sulphide group may require to be separated by the use of ammonium sulphide before proceeding to the determination of lime and magnesia. In such cases the members of the ammonium sulphide group must be separated by methods which will be suggested later. The precipitate with ammonium sulphide may carry with it some lime on account of the absorption of carbonic acid by the reagent. Wash off with a little acetic acid to dissolve adhering lime, treat

the acetic washings again with an excess of ammonium sulphide, filter, and add this filtrate to the main solution in which the lime and magnesia are to be determined, and continue in the usual manner.

Chlorine.—Titration with tenth normal silver nitrate (with potassium chromate indicator) is employed. With most mineral waters portions of 25 c. c. will suffice. If the water is not neutral it must be made so by addition from a burette of tenth normal alkali or tenth normal acid (nitric or sulphuric), using methyl orange indicator. A separate portion of the water should be used in order to decide how much alkali or acid will be necessary to effect neutrality, as it is not advisable to make the silver titration on a sample containing the methyl orange indicator.

If the water contains hydrogen sulphide it will be necessary to add to some measured amount, after neutralizing, a few drops of solution of pure copper sulphate, avoiding the use of any decided excess, and then to filter. After washing the precipitate of copper sulphide free from chlorides, proceed with the titration.

It will be perceived that if bromides or iodides are present, all three halogens will be estimated together.

After determining the iodine and bromine by methods to be described, a correction must be calculated and applied in order to get the true amount of chlorine present in the chlorides.

Sulphuric Acid.—The amount of water to be taken will depend upon the intensity of the reaction shown by a qualitative test with barium chloride on the acidified water. It is usually inadvisable to take more than 1 litre; in some cases 200 c. c. will suffice. Acidulate with hydrochloric acid, concentrate if necessary to 150 to 200 c. c., and precipitate by barium chloride, with the usual precautions (see analysis of magnesium sulphate). In the case of sulphur waters, a special method, to be described later, should be applied.

Alkalies.—Acidify 1 litre of the water with hydrochloric acid, and evaporate to dryness in a platinum dish. Redissolve in about 50 c. c. of water containing a few drops of hydrochloric acid, add solution of barium hydrate in quantity sufficient to completely precipitate all magnesia, etc. (gelatinous precipitate), boil and filter. (The barium hydrate may possibly contain alkalies, and should be tested before use.) In the filtrate, precipitate out the barium in the cold by ammonium carbonate and ammonia, and filter. To the filtrate add excess of sulphuric acid, filter if necessary, evaporate to dryness in platinum and ignite off ammonia salts, excess of acid, and to destroy organic dust, which is likely to have accumulated in the solution during the previous operations. A repetition of the treatment with barium hydrate at this stage is desirable, after adding enough barium chloride to reconvert all the bases to chlorides, in order to remove the last traces of magnesia. After the ignition with sulphuric acid, sprinkle the residue with powdered ammonium carbonate and ignite again, cool, and weigh. The residue should now consist exclusively of potassium and sodium sulphates, and be entirely soluble in water. Determine the potassium by the Lindo-Gladding method, calculate to sulphate, deduct from the weight of the mixed sulphates, and calculate from the remainder taken as sodium sulphate the weight of the soda.

Lithia.—If 10 c. c. of the original water, when evaporated to dryness, gives a strong persistent lithia line when tested by the spectroscope, 250 to 500 c. c. will suffice for this determination. If, as is usually the case, the lithium is present in smaller proportion, larger quantities must be evaporated.

To test qualitatively for lithia, evaporate some of the water, moisten the residue with hydrochloric acid, and heat again, cool, and then pour over the residue 20 c. c. of a mixture of equal volumes of alcohol and ether, stir well, decant through a filter, and evaporate the solution

in a small capsule, moisten with hydrochloric acid and test by the spectroscope.

If 10 litres of the water treated in this manner afford only a weak evanescent lithia line, it will be useless to attempt the separation, and only a "trace" of lithia can be reported. With waters stronger in lithia, evaporation of an amount sufficient to give a decided lithia line when acidified and concentrated to about 50 c. c. will usually suffice.

To determine the lithia treat as follows: Evaporate the amount found to be necessary, after acidification with hydrochloric acid, to dryness, take up with acidulated water, precipitate by barium hydrate solution, and filter and wash. Separate the remaining barium by ammonia and ammonium carbonate, filter, evaporate to dryness, and expel ammonium salts by cautious ignition. In igniting at this stage it may be found necessary to cover the dish with a round of filter-paper to prevent loss by the decrepitation of the chlorides in parting with the last portions of water. Dissolve the residual chlorides in acidulated water, and repeat the treatment with barium hydrate, ammonium carbonate, etc., to obtain the pure chlorides. Throughout these operations frequent tests must be made with the spectroscope to insure against loss of lithia, and all precipitates, etc., must be washed until the spectroscope test shows that little or no lithia remains in the portions rejected.

Barium sulphate, which may occur in the first precipitate with barium hydrate, always carries lithia with it, which washes out with some difficulty. Lithium hydrate, which may also be in this precipitate, is not very soluble in water. Lithium carbonate is still less soluble, and may adhere to the barium carbonate precipitate with great persistency. With the latter, time and labor may be saved by washing the barium carbonate only moderately, then dissolving in as little hydrochloric acid as possible, and reprecipitating with ammonia and ammonium-

carbonate. It must also be remembered that lithium chloride solutions on evaporation are prone to form some difficultly soluble compound of lithia (oxide, hydrate, or oxychloride) by loss of chlorine, and where circumstances will allow should be kept slightly acid with hydrochloric acid.

If the alkaline chlorides, obtained as described, amount to 0.2 gm. or less they may be treated at once with amyl alcohol. If over 0.2 gm., concentrate the lithia by digesting the chlorides two or three times with a mixture of equal bulks of alcohol and ether, acidified with a drop of hydrochloric acid. Filter off the solution each time, and repeat the treatment until the insoluble portion shows no lithia. Evaporate off the alcohol and ether, and extract the residue with amyl alcohol by Gooch's method (*Am. Chem. Jour.*, IX., 33), viz.: Dissolve in a small casserole in a very little acidulated water, add about 30 c. c. of pure *anhydrous* amyl alcohol, and heat on a sand-bath with a low flame, so as to boil off the water through the amyl alcohol, and afterward to boil off some of the amyl alcohol itself (128° to 132° C). Keep up the heat until the volume of the amyl alcohol has been reduced to 15 or 20 c. c. Add two drops of hydrochloric acid, and boil again for half a minute. Cool, and then pour the solution through a small filter (a Gooch crucible having as filtering bed a small paper disk or a thin layer of asbestos), receiving the filtrate in a measuring cylinder. Note the volume. Dissolve the alkaline chlorides again in a little water, and repeat the extraction with amyl alcohol, noting the volume as before. Unite the amyl alcohol solutions and evaporate down in a weighed platinum dish. Meantime wash the casserole and filter with cold amyl alcohol until the washings show no lithia, and evaporate the washings with the main solution. After driving off the amyl alcohol moisten the residue of lithium salt (chiefly chloride) with pure sulphuric acid, evaporate to dryness, and then raise the heat cautiously until it is brought to that of intense ignition. Cool and weigh.

From the weight of the sulphates a deduction must be made for potassium and sodium chloride dissolved by the amyl alcohol, which was *boiled* in contact with the chlorides. The *cold* amyl alcohol used for washing dissolves practically none.

From the weight of the sulphates, for every 10 c. c. of amyl alcohol which remained in contact with the chlorides after heating deduct as follows:

When only NaCl and LiCl were present...0.00050 gm.

“ “ KCl and LiCl “ “ ...0.00059 “

When all three were present.....0.00109 “

The remainder is taken as Li_2SO_4 , and calculated accordingly.

For *Barium*, *Strontium*, *Iodine*, *Bromine*, etc., proceed as follows:

Evaporate 5 to 15 litres of (the alkaline) water nearly to dryness.

EXTRACT WITH WATER.

<i>Residue A.</i> Treat with HCl, and evaporate to dryness. Take up with HCl and water.	<i>Solution A.</i> Neutralize. Fractional precipitation with AgNO_3 .	
<i>Residue B.</i> SiO_2 , BaSO_4 , SrSO_4 , etc.	<i>Solution B</i> + solution from <i>Residue B.</i> Divide in halves.	<i>Precipitation C,</i> <i>Solution C,</i> for B_2O_3 (Gooch's distillation method).
Expel SiO_2 by HFl, etc.; fuse residue of sulphates with NaK CO_3 ; extract with water, and dissolve residue in HCl; add to solution B.	Half for Fe, Al, and Mn (possibly Zn, Ni, Co, etc.).	Half fractional precipitation by H_2SO_4 .
	<i>Precip.</i> for Ba and Sr.	<i>Sol'n</i> for P_2O_5 .

In evaporating the necessary quantity of water it is indispensable that the alkalinity of the solution should be maintained. If it becomes acid, there will be a loss of iodine, bromine, and boracic acid. With waters of the character of the Saratoga waters no addition of sodium carbonate will be necessary. In the case of acid or neutral waters, sodium carbonate must be added. In the

special case of waters containing much magnesium chloride it may occur that the water is rendered acid by concentration, and such waters should be tested as to alkalinity from time to time during evaporation.

The treatment described for Residue B explains itself, the intention being, after removing the silica to obtain the barium and strontium (possibly iron and alumina) in solution, which is to be combined with solution B for further treatment. In the half of this solution devoted to the determination of iron, etc., the methods described in the analysis of ores of iron, manganese, zinc, etc., must be used; *e. g.* separate iron and alumina by basic acetate separation, and in the filtrate, slightly acid with acetic, precipitate out zinc, nickel, etc., by hydrogen sulphide if necessary, and in the filtrate from this, after boiling out hydrogen sulphide, separate the manganese by bromine. In alum waters it will be necessary to evaporate the filtrate from the basic acetate precipitation nearly or quite to dryness, and to take up with a little dilute acetic acid in order to insure the complete separation of the alumina.

The basic acetate precipitate should be dissolved in hydrochloric acid, and the iron and alumina precipitated out with ammonia, washed, etc., and weighed, when it may again be dissolved by fusion with potassium bisulphate, and the iron titrated in the usual manner, the alumina being determined by difference. Phosphoric acid if present, as well as ferric oxide, must be deducted to get the true weight of the alumina.

In the other half, which should be fairly concentrated, sulphuric acid must be added in sufficient quantity to precipitate all of the barium and strontium, and a little only of the lime. The bases in this precipitate must be brought into solution in the same manner as before; by fusion with alkaline carbonate, and extracting with water, which leaves the alkaline earth carbonates. These are then to be dissolved in a little acetic acid, and in the solution the barium is precipitated by potassium chromate, in

which form it can be dried and weighed, or it may be digested with sulphuric acid, and converted into sulphate for weighing.

The solution containing calcium and strontium should be precipitated with ammonium carbonate, the precipitate washed and dissolved in a little nitric acid, this solution evaporated to dryness in a small weighed capsule, and the residue extracted with alcohol and ether. The residue of strontium nitrate may be evaporated with sulphuric acid, ignited, and the strontium sulphate weighed. Test with the spectroscope.

To the portion filtered from the alkaline earth sulphates add a little ferric chloride, precipitate with ammonia, dissolve the precipitate in nitric acid, and separate phosphoric acid by means of molybdate solution.

Solution A must be rendered neutral or slightly acid with nitric acid. Then run in slowly with vigorous stirring enough silver nitrate solution (twentieth to fiftieth normal) to more than precipitate all the iodide and bromide present. Roughly estimated this would be about 20 c. c. of fiftieth normal solution for each litre assumed to contain 1 part of alkaline bromides and iodides per hundred thousand. The amount may be judged by a qualitative test. Under these conditions the bromide and iodide react first with the silver, a portion of the silver chloride formed dissolving in the excess of alkaline chloride. Allow the precipitate to settle in some place where it is protected from the light, decant off the solution when absolutely clear, and filter the precipitate through a small filter. Wash, and when thoroughly washed, punch a hole in the paper, rinse the precipitate into a weighed porcelain capsule, dry thoroughly, heat to *incipient* fusion, and weigh the mixed iodide, bromide, and chloride. Protect these silver salts from strong light throughout. Then cover the mass with very dilute sulphuric acid, add a few granules of metallic zinc at least three times the weight of the precipitate, and allow the reaction to go on until only metallic sil-

ver is left. Pour off the solution, which now contains zinc iodide, bromide, and chloride, reserving it with the first washings for the determination of the iodine. Wash the silver alternately with ammonia and with warm dilute hydrochloric acid, throwing those washings away. Then dry and ignite the metallic silver and weigh.

In the solution containing the zinc salts *nearly* neutralize with sodium hydrate, and precipitate iodine by means of palladium chloride, as PdI_2 , weighing finally the metallic palladium (see analysis of Potassium Iodide).

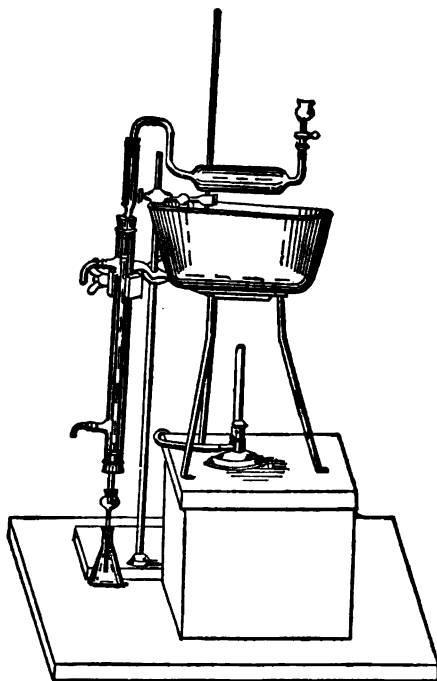
Calculate the iodine equivalent to the palladium. Calculate also the amount of silver iodide, and the amount of silver to which it is equivalent. Deduct these amounts respectively from the weights of silver salts and of metallic silver obtained above. The remainders show respectively the weights of mixed silver chloride and bromide, and of the silver therefrom.

The weight of the bromine present can then be found by the proportion

$\text{AgBr} - \text{AgCl} (44.5) : \text{Br} (80) = \text{Wt. of mixed silver salts less Ag, calculated as chloride} : \text{Wt. of bromine present.}$

Solution C is to be treated for boric acid by Gooch's method (*Am. Chem. Jour.*, IX. 23). Render alkaline by sodium carbonate and evaporate to dryness. Transfer the salts to a small flask, which is arranged so that it can be heated in a paraffine bath, and is connected with a condenser. The end of the condenser is attached to a small Erlenmeyer flask, by means of a thistle tube and a rubber stopper grooved to permit the free passage of air. Instead of a flask Gooch recommends the form of receptacle ("re-tort") represented in the figure, which will be advantageous when the mass of salts to be treated is not very large. The dried salts are treated with acetic acid and methyl alcohol, which latter on being distilled off carries the boric acid with it. The acid is caught in milk of lime contained in the Erlenmeyer flask. About 1.5 gm. of

pure lime in a platinum dish is heated with a strong flame, and finally over a blast-lamp for 5 minutes, cooled in a desiccator, and weighed. It is then slaked by addition of a little water and rinsed into the Erlenmeyer flask. To the salts in the flask or "retort" is added a slight excess of



acetic acid, and the vessel is heated in the paraffine bath until it becomes dry. Then 10 c. c. of methyl alcohol are added, the flask closed, and the alcohol distilled over into the lime. Another 10 c. c. of methyl alcohol is added, and distilled over, the operation being repeated at least six times, using 10 c. c. of methyl alcohol each time. At about the fourth distillation, a few drops of acetic acid should be added along with the methyl alcohol, to keep the contents of the "retort" from becoming alkaline.

When the contents shows no reaction for boric acid by the turmeric-paper test (red coloration on drying off) rinse the contents of the receiver (Erlenmeyer flask) into a platinum dish by the aid of a little water, boil off the methyl alcohol, and evaporate to complete dryness. Ignite the lime in the same manner as before the distillation. Repeat the ignition until a constant weight is obtained. The increase in weight is due to boric anhydride (B_2O_3).

Fluorine.—Evaporate four or five litres of the water to small bulk, adding sodium carbonate if necessary to keep the solution alkaline. Precipitate hot with calcium chloride, filter, wash, dry and ignite, and then treat with acetic acid to dissolve off carbonates, etc. Dry the residue thoroughly, and treat it with pulverized quartz and strong sulphuric acid in the manner described (note to Chapter V., Calcium Fluoride).

Calculation of the Analysis.—The sulphuric acid is combined with potassium to form sulphate.

The potassium unsatisfied by sulphuric acid is combined with chlorine to form potassium chloride.

The chlorine not required by potassium is combined with sodium to form sodium chloride.

The bromine, iodine, phosphoric acid, boracic acid, and nitric acid are combined with sodium, to form bromide, iodide, phosphate, baborate, and nitrate.

The sodium bicarbonate is determined directly.

The sodium is not determined, but is assumed as the sum of all required to combine with chlorine, bromine, iodine, phosphoric acid, boracic acid, nitric acid, and carbonic acid.

The lithium, magnesium, calcium, less that for fluorine, strontium, barium, iron, and manganese, are combined with carbonic acid to form bicarbonate.

The fluorine is calculated to calcium fluoride.

The alumina, silica, and organic matter are reported as such.

Sulphur Waters.—The constituents of these waters are very similar to those found in most spring waters, with

the exception of the sulphur compounds, as will be seen by the subjoined report of analyses of the waters of Chittenango, Madison Co., N. Y., taken from a lecture of Dr. C. F. Chandler, published in *Am. Chem.*, December, 1871.

ANALYSIS OF SULPHUR WATERS.

IN ONE U. S. GALLON OF 231 CUBIC INCHES.	CHITTENANGO, MADISON COUNTY, N. Y.			
	White Sulphur Sp'g.	Cave Spring.	Magnesia Spring.	Florida Spring, Montgomery Co., N. Y.
	Grains.	Grains.	Grains.	Grains.
Hydrosulphate of sodium, NaHS.....	0.117	0.886	0.757	2.008
Hydrosulphate of calcium Ca (HS) ₂	1.128	0.929
Sulphate of potassa.....	1.890
Sulphate of soda.....	0.218
Sulphate of lime.....	81.420	106.126	115.085
Sulphate of strontia.....	Trace.	Trace.	Trace.
Sulphate of magnesia.....	1.953	7.589	12.718
Hyposulphite of soda.....	0.257	0.020	0.711
Bicarbonate of soda, NaHCO ₃	22.148
Bicarbonate of lime.....	8.817
Bicarbonate of magnesia.....	22.017	28.973	20.779	6.972
Bicarbonate of iron.....	0.078	0.156	0.325
Chloride of potassium.....	0.156	0.233	0.333
Chloride of sodium.....	1.037	1.569	1.833	5.890
Chloride of lithium.....	Trace.	Trace.	Trace.
Alumina.....	0.082	0.222	Trace.	Trace.
Silica.....	0.286	0.519	0.577	0.793
Sulphur (in suspension).....	Trace.
Sulphide of iron (in suspension).....	0.176
Total solid contents per gallon	107.859	142.118	158.856	43.890
Total sulphur in the metallic sulphides and sulphuretted hydrogen.....	0.339	1.897	2.400	1.9165
CUBIC INCHES OF GAS PER GALLON.				
Sulphuretted hydrogen gas....	0.884	2.754	5.623	8.765
Carbonic acid gas.....	20.490	15.934	19.456	32.169

"The analyses were made in the Editor's laboratory, with the assistance of W. H. Chandler and F. A. Cairns."

The evaporation of large quantities of the water, and the determinations of the ordinary constituents are made in the way directed in analysis of Saratoga water.

Sulphur Compounds.—The following extract from the *Chem. News, American Supplement*, April, 1870, gives

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**THE FOLLOWING STATEMENT OF ANALYSES OF SARATOGA WATER IS
LER, AND PUBLISHED IN THE
ANALYSES OF SOME OF THE SPRINGS AND**

COMPOUNDS AS THEY EXIST IN SOLUTION IN THE WATER.	IN SAR.					
	Star Spring.	High Rock Spring.	Seltzer Spring.	Pavilion Spring.	United States Spring.	Hathorn Spring.
Chloride of sodium.....	398.361	390.127	134.291	459.903	141.872	509.968
Chloride of potassium.....	9.695	8.974	1.335	7.660	8.824	9.597
Bromide of sodium.....	0.571	0.731	0.630	0.987	0.844	1.534
Iodide of sodium.....	0.126	0.086	0.031	0.071	0.047	0.198
Fluoride of calcium.....	Trace.	Trace.	Trace.	Trace.	Trace.	Trace.
Bicarbonate of lithia.....	1.586	1.967	0.899	9.486	4.847	11.447
Bicarbonate of soda.....	12.662	34.888	29.428	3.764	4.668	4.288
Bicarbonate of magnesia.....	61.912	54.924	40.339	76.267	72.883	176.463
Bicarbonate of lime.....	124.459	131.739	89.869	120.169	93.119	170.646
Bicarbonate of strontia.....	Trace.	Trace.	Trace.	Trace.	0.018	Trace.
Bicarbonate of baryta.....	0.066	0.494	Trace.	0.875	0.909	1.737
Bicarbonate of iron.....	1.213	1.478	1.703	2.570	0.714	1.128
Sulphate of potassa.....	5.400	1.608	0.557	2.032	Trace.	Trace.
Phosphate of soda.....	Trace.	Trace.	Trace.	0.007	0.016	0.006
Borate of soda.....	Trace.	Trace.	Trace.	Trace.	Trace.	Trace.
Alumina.....	Trace.	1.223	0.374	0.329	0.064	0.131
Silica.....	1.283	2.260	2.561	3.155	3.184	1.260
Organic matter.....	Trace.	Trace.	Trace.	Trace.	Trace.	Trace.
Total per U. S. gal., 231 cu. in.	617.367	630.500	302.017	687.275	331.837	888.403
Carbonic acid gas.....	407.650	409.458	324.080	332.458	245.734	375.747
Density.....	1.0091	1.0092	1.0034	1.0095	1.0035	1.0115
Temperature.....	52° F.	52° F.	50° F.	50°

BASES AND ACIDS, AS ACTUALLY I

Potassium.....	7.496	5.419	0.949	4.931	4.515	5.024
Sodium.....	160.239	163.216	61.003	182.084	57.259	202.058
Lithium.....	0.163	0.202	0.093	0.976	0.499	1.179
Lime.....	43.024	45.540	31.066	41.540	32.189	58.989
Strontia.....	Trace.	Trace.	Trace.	Trace.	0.009	Trace.
Baryta.....	0.056	0.292	Trace.	0.517	0.537	1.028
Magnesia.....	16.992	15.048	11.051	20.895	19.968	48.246
Protoxide of iron.....	0.491	0.596	0.689	1.040	0.289	0.456
Alumina.....	Trace.	1.223	0.374	0.329	0.064	0.131
Chlorine.....	246.357	241.017	82.128	282.723	90.201	314.037
Bromine.....	0.445	0.568	0.489	0.767	0.656	1.188
Iodine.....	0.106	0.072	0.026	0.060	0.039	0.166
Fluorine.....	Trace.	Trace.	Trace.	Trace.	Trace.	Trace.
Sulphuric acid (SO ₃).....	2.483	0.739	0.156	0.834	Trace.	Trace.
Phosphoric acid (P ₂ O ₅).....	Trace.	Trace.	Trace.	0.004	0.008	0.003
Boric acid.....	Trace.	Trace.	Trace.	Trace.	Trace.	Trace.
Carbonic acid (CO ₂) in carbonates.....	56.606	62.555	44.984	60.461	50.380	104.928
Carbonic acid (CO ₂) for bicarbonates.....	56.606	62.555	44.984	60.461	50.380	104.928
Silica.....	1.283	2.260	2.561	3.155	3.184	1.260
Organic matter.....	Trace.	Trace.	Trace.	Trace.	Trace.	Trace.
Water in bicarbonates.....	23.180	25.591	18.405	24.736	20.613	42.928
Oxygen in K ₂ SO ₄	0.946	0.148	0.051	0.187
Oxygen in LiHCO ₃	0.187	0.232	0.105	1.116	0.570	1.347
Oxygen in NaHCO ₃	1.206	3.232	2.803	0.358	0.444	0.408
Oxygen in Na ₂ HPO ₄	0.001	0.002	0.001
Total per U. S. gal., 231 cu. in.	617.367	630.500	302.007	687.275	331.837	888.403
Total residue by evaporation.	537.600	542.350	238.070	602.080	290.840	740.550

These analyses have been made from time to time during the past ten years, some of them by chemists: M. Alsberg, Ph. D., E. W. Root, A. M., Paul Schweitzer, Ph. D., W. H. Candler, Ph. D., E. M.

TAKEN FROM A LECTURE ON WATER, DELIVERED BY DR. C. F. CHAND.
 ILLINOIS. CHEMIST, DECEMBER, 1871.

ARTESIAN WELLS OF SARATOGA COUNTY, N. Y.

OGA.							IN BALLSTON.		
Well.	Congress Spring.	Geyser Spouting Well.	Vichy.	Union.	Empire Spring.	Glacier Spouting Well.	Ballston Artesian Lithia Well.	Franklin Artesian Well.	Conde Dentonian Well.
68	400'444	562'080	128'689	458'299	506'630	702'239	750'030	659'344	645'481
27	8'049	24'634	14'113	8'733	4'292	40'446	33'276	33'630	9'232
14	8'559	2'212	0'990	1'307	0'266	3'579	3'643	4'065	2'368
66	0'138	0'248	Trace.	0'039	0'606	0'234	0'124	0'235	0'225
ce.	Trace.	Trace.	Trace.	Trace.	Trace.	Trace.	Trace.	Trace.	Trace.
26	4'761	7'004	1'760	2'605	2'080	6'247	7'750	6'777	10'514
64	10'775	71'232	82'873	17'010	9'022	17'624	11'928	94'604	34'400
61	121'757	149'343	41'503	109'685	42'953	183'972	180'602	177'868	158'349
81	143'399	170'392	95'522	96'703	109'656	227'070	238'156	232'332	178'484
ce.	Trace.	Trace.	Trace.	Trace.	Trace.	Trace.	Trace.	Trace.	Trace.
28	0'928	2'014	0'593	1'703	0'070	2'083	3'881	1'231	4'739
26	0'340	0'879	0'052	0'269	2'769	0'647	1'581	1'609	2'269
58	0'889	0'318	Trace.	1'818	2'769	0'252	0'520	0'762	Trace.
09	0'016	Trace.	Trace.	0'026	0'023	0'010	0'050	0'011	0'003
ce.	Trace.	Trace.	Trace.	Trace.	Trace.	Trace.	Trace.	Trace.	Trace.
05	Trace.	Trace.	Trace.	0'324	0'418	0'458	0'077	0'263	0'365
13	0'840	0'665	0'758	2'653	1'458	0'699	0'761	0'735	1'026
ce.	Trace.	Trace.	Trace.	Trace.	Trace.	Trace.	Trace.	Trace.	Trace.
55	700'895	991'546	367'326	701'174	680'436	1,195'582	1,233'246	1,184'368	1,047'700
52	392'289	454'082	383'071	384'909	344'069	465'456	428'114	460'066	358'345
60	1'096	1'0120	1'0159	1'0135	1'0125
	52° F.	46° F.	50° F.	48° F.	52° F.	52° F.	49° F.

FOUND IN THE ANALYSES, UNCOMBINED.

26	4'611	13'039	7'400	5'487	3'492	21'312	17'653	18'104	4'833
06	162'324	251'031	73'507	185'150	202'945	281'758	299'005	286'221	263'769
45	0'490	0'720	0'181	0'268	0'214	0'643	0'798	0'668	1'082
18	49'569	58'901	33'020	33'428	37'906	78'493	82'328	69'942	61'696
ce.	Trace.	0'211	Trace.	Trace.	0'040	0'430	0'001	0'094
20	0'549	1'190	0'350	1'007	0'041	1'230	2'292	0'727	2'799
92	33'358	40'915	11'370	30'050	11'768	53'142	49'480	48'731	43'883
24	0'137	0'396	0'021	0'109	0'321	0'263	0'639	0'651	0'929
5	Trace.	Trace.	0'473	0'324	0'418	0'458	0'077	0'263	0'395
2	246'834	352'825	84'807	282'175	308'357	445'392	470'997	416'278	396'096
22	6'645	1'718	0'769	1'015	0'107	2'780	2'829	3'623	1'839
55	0'117	0'208	Trace.	0'033	0'513	0'198	0'104	0'197	0'189
ce.	Trace.	Trace.	Trace.	Trace.	Trace.	Trace.	Trace.
92	0'409	0'146	Trace.	0'835	1'272	0'115	0'239	0'350	Trace.
04	0'008	Trace.	Trace.	0'013	0'011	0'005	0'025	0'006	0'002
ce.	Trace.	Trace.	Trace.	Trace.	Trace.	Trace.	Trace.
84	80'249	112'880	60'840	64'974	45'972	127'298	125'973	136'133	110'019
84	80'249	112'880	60'839	64'974	45'972	127'298	125'973	136'133	110'019
13	0'840	0'065	0'758	2'653	1'458	0'699	0'781	0'735	1'026
ce.	Trace.	Trace.	Trace.	Trace.	Trace.	Trace.	Trace.
96	33'828	46'183	24'891	26'587	18'720	52'077	51'543	55'696	45'013
90	0'082	0'029	0'167	0'254	0'023	0'048	0'070
09	0'563	0'824	0'307	0'302	0'215	0'735	0'911	0'797	1'237
59	1'024	6'785	7'893	1'620	0'859	1'678	1'136	9'011	3'277
ce.	0'002	0'003	0'005	0'001	0'006	0'001	Trace.
55	700'895	991'546	367'326	701'174	680'436	1,195'582	1,233'246	1,184'368	1,047'700
70	588'818	832'483	281'595	609'613	1,055'730	992'540	892'670

by the writer alone; most of them, however, with the assistance of one or more of the following
 A. Cairns, A. M., F. Bruckmann, E. M., Walter Jenney, E. M., L. R. Nettre, E. M., R. S. Robert

the method of determining the sulphur compounds: "The method employed for determining the sulphur compounds was a modification of the one employed by Simmler in the analysis of the Stachelberg water, the account of which was published in *Erdmann's Journal*, Vol. LXX. The alterations introduced lessen to a great extent the amount of analytical work to be done at the spring. The following brief statement may prove of interest:

"1. In a glass-stoppered bottle, to one litre of water was added an excess of neutral solution of nitrate of silver.

"2. To another litre was added an excess of a solution of chloride of cadmium.

"3. Through a third litre pure hydrogen was transmitted until the gas, after passing through the water, no longer decolorized a dilute solution of iodide of starch. An excess of a solution of chloride of cadmium was then added.

"These three bottles were well agitated, securely sealed, and transported to the laboratory. From each, the precipitate was filtered, washed, dissolved, and oxidized by fuming nitric acid and potassium chlorate, filtered, and the sulphuric acid determined in the filtrate with barium chloride.

"No. 1. This precipitate contained the sulphur, existing in the form of sulphides and hyposulphites.

"No. 2. Contained the sulphur existing in the form of sulphides, including the free sulphuretted hydrogen.

"No. 3. Contained the sulphur present in the form of sulphuretted sulphides. The difference between No. 3 and No. 2 indicated the amount of sulphur as free sulphuretted hydrogen; and by deducting No. 2 from No. 1, the amount of hyposulphites was ascertained.

"In the original filtrate from No. 1, the sulphuric acid was determined, after removing the excess of silver by hydrochloric acid."

The changes made in Simmler's method were suggested by Wm. H. Chandler. Bromine may be used instead of

nitric acid and potassium chlorate in oxidizing the precipitates containing sulphur.

Sulphuretted waters should be examined without delay, especially as to their contents in sulphides, hyposulphites, etc. On standing, even for a day, changes in those compounds will occur, so that an analysis made on a water after standing for a few days will show very different results, as regards those constituents, from those obtained on the water when fresh from the spring. Not only does hydrogen sulphide escape, but the proportion of sulphides diminishes, while that of hyposulphite increases.

CHAPTER XXXIV.

ACIDIMETRY AND ALKALIMETRY.

The solutions employed are of sulphuric, hydrochloric, nitric, or oxalic acid, and of sodium, potassium, or ammonium hydrate, or sodium carbonate. Besides these it is necessary to have solutions of some coloring matters, called indicators, which show a decided change of color when the solution in which they are contained pass from an alkaline to an acid condition, or *vice versa*.

"Normal Solutions."—In this work, by a normal solution is meant one which contains as many grams per litre of the substance as there are units in the molecular weight; *e. g.*, normal solutions of H_2SO_4 , of HNO_3 , of NaOH , or Na_2CO_3 , contain respectively 98, 63, 40, and 106 grms. of material per litre.

Note.—Sutton's *Handbook of Volumetric Analysis*, which is regarded as a standard in England, defines a normal solution (5th ed., p. 22) as one so prepared "that one litre at 16°C . shall contain the *hydrogen equivalent* of the active reagent weighed in grams ($\text{H} = 1$).” According to this definition the normal solutions of H_2SO_4 or Na_2CO_3 would be half of the strength above mentioned, while those of HNO_3 or NaOH would be the same as already given.

Fractional normal, as half-normal, fifth-normal, tenth-normal solutions, etc., designated as $\text{N}/2$, $\text{N}/5$, $\text{N}/10$, etc., are frequently used in some cases, where they may be found convenient.

Advantages.—The advantages of normal or fractional normal solutions consists in the fact that being made up in reference to molecular weights, the standard may be readily known in terms of any substance on which they

may be used. For instance: 1 c. c. normal HCl containing 0.0365 gm. HCl will neutralize 0.04 gm. NaOH, 0.047 KOH, 0.017 NH_3 , 0.053 Na_2CO_3 , etc., the molecular weights being NaOH = 40, KOH = 56, NH_3 = 17, Na_2CO_3 = 106 (one half = 53, since it contains Na, etc., etc.; or 1 c. c. normal KOH containing 0.047 gm. KOH will neutralize 0.049 gm. H_2SO_4 , 0.063 gm. HNO_3 , 0.060 gm. $\text{HC}_2\text{H}_3\text{O}_2$, etc., the molecular weight of each giving the standard at once.

Use of Normal Solutions.—These may be used in an “absolute” or in what may be termed a “relative” manner. Used “absolutely,” the absolute amount of acid in any solution may be determined; *e. g.*, suppose a given solution known to contain caustic potash is found to require 23 c. c. of half-normal sulphuric acid to exactly neutralize it. It must therefore contain $23 \times 0.047 = 1.081$ grms. KOH.

In what is here termed the “relative” use, the material analyzed is weighed out in such proportion that the burette reading gives percentage at once without calculation; *e. g.*, suppose we have a sample of crude caustic potash, the impurities of which are either insoluble or neutral to indicators. If we weigh out 4.7 grms. (one tenth the molecular weight) and extract with water, the *number of* c. c. of normal hydrochloric or half-normal sulphuric acid required to neutralize the solution gives the *percentage* of KOH present. Were it pure, 100 c. c. would be required; if 50 per cent, 50 c. c.; 23 per cent, 23 c. c.; etc. The reason is obvious.

Of course, if the substance were crude carbonate, K_2CO_3 , one twentieth of the molecular weight (6.9 grms.) would have to be weighed out, since the formula shows K_2 .

Indicators.—A variety of different coloring matters have been proposed and used for this purpose. Each one of these has its peculiar advantages and its defects. An acquaintance with the properties of the different indicators is of great service in the practice of alkalimetry

and acidimetry. Only the principal ones can be here mentioned.

1. *Litmus*.—Prepared from lichen (*Rocella tinctoria*). *Acid* red. *Alkaline* blue. The oldest indicator. The commercial article contains calcium carbonate, used in preparing, and sometimes indigo as an adulterant. Different lots give indicators of somewhat different qualities. To prepare the commercial article for use (Sutton) dissolve in water, evaporate somewhat, then add acetic acid to neutralize carbonate, etc. Evaporate to a syrup, extract the impurities with strong alcohol, and then dissolve the purified color in water. The solution loses color unless exposed to the air.

Useless in gas or lamp light. With sodium light, however, it can be used. In that case when acid a solution appears colorless, when alkaline like diluted ink. (L d'Henry, *Compt. Rend.*, LXXVI., 222.) Unsatisfactory in presence of CO_2 , SO_2 , CrO_3 , organic acids or salts of iron, alumina, etc.

2. *Cochineal* (Carminic acid).—Prepared from the cochineal insect. *Acid* reddish yellow. *Alkaline* red violet. To obtain a solution for laboratory use the pulverized insects are first extracted with ether to remove fatty matter, and then digested with alcohol (of 25 to 30 per cent), which takes up the color. Unaffected by small amounts of carbonic acid. Unsatisfactory in presence of organic acids, ferric or aluminic salts, etc. Destroyed by hot alkaline solutions even when very dilute.

3. *Turmeric* (Curcumin).—Prepared from the root of *Curcuma longa*. *Acid* yellow. *Alkaline* brown. The tint is different for carbonated or caustic alkali. (Siegwart, *Ch. Centr.*, 74, 302.) The dried root is cut in small pieces, first digested with a little water, and then the color is extracted with alcohol (of 50 per cent). Used almost invariably on paper. Indistinct with H_2S , carbonic, boracic, silicic, phosphoric, and some organic acids.

Thomson finds it very satisfactory with tartaric acid and citric acids, etc.

4. *Rosolic Acid* (Coralline).—Prepared by heating together phenol, sulphuric acid, and oxalic acid (3 : 2 : 2) to 140°–150° C. *Acid* yellow. *Alkaline* cherry red. Dissolved in alcohol (of 50 per cent) for use. Slow in presence of ammonia or its salts, also with many acids, as phosphoric, silicic, etc. Affected by CO₂, neutral to bicarbonates. Tolerably good with tartaric acid, less satisfactory with citric, acetic acids, etc.

5. *Phenol-Phthalein*.—Prepared by heating together phenol, phthalic anhydride, and sulphuric acid (20 : 1 : 8) 10 to 12 hours at 115° to 120°. *Acid* colorless. *Alkaline* bright crimson. Dissolved in alcohol (of 50 per cent) for use. Useless with ammonia and its salts. Sensitive to CO₂ and H₂S, etc. Neutral to bicarbonates and alkaline sulphides of RHS type. Good for organic acids. Neutral to Na₂HPO₄, etc., and to the corresponding arsenic compounds. Works well in artificial light.

6. *Phenacetolin*.—Prepared by heating together phenol, sulphuric and acetic acids (94 : 98 : 60). *Acid* golden yellow. *Alkaline* faint yellow. With alkaline carbonates it shows a dark pink, with bicarbonates an intense pink. Serviceable with carbonates. Slow with sulphites, useless with arsenic acids. This indicator is but little used in the United States, though it is much liked by some English analysts.

7. *Lakmoid*.—Prepared by heating together resorcin, KNO₃, and a little water (20 : 1 : 1) to 110° to 120°. *Acid* red. *Alkaline* blue. Dissolved in alcohol (of 50 per cent) for use. Unaffected by small amounts of CO₂, useless in presence of H₂S or sulphides. Uncertain with organic acids.

8. *Methyl Orange* (Poirrier Orange, No. III, Tropæolin D, Helianthin, Roassin).—Ammonia salt of di-methyl-amido-azo-benzene-sulfo acid. Prepared by the action of diazo-sulfanilic acid on dimethylanilin. *Acid* cherry-red.

Alkaline yellow. Dissolved in water for use, solubility in water small. Not affected by moderate amounts of carbonic acid. Poor for organic acids. Decomposed and rendered useless by oxalic acid or oxalates. Neutral to ferric and aluminic salts, also to calcium bisulphite, NaH_2PO_4 , etc. Works best when used in very small amounts in *cold* solutions.

9. *Congo Red* (Sodium salt of benzidin-diazo-naphthionic acid).—*Acid* blue. *Alkaline* red. Dissolved in water for use. Unaffected by small amounts of CO_2 or organic acids. Neutral to ferric, aluminic, and many other similar salts. Works very well on paper, which it dyes directly, having affinity for cellulose. Like methyl orange, it should be used only in small amounts. Thomson condemns it as lacking delicacy.

For more complete information on the use of indicators consult papers by Thomson (*Chem. News*, XLVII., 123, 135, 184; XLIX., 32, 38, 119; and LII., 18, 29), also *Jour. Soc. Chem. Ind.*, VI, 196. The quality of these indicators when obtained from dealers is often unsatisfactory; each new lot should be tested. It is advisable to use definite proportions of indicator, in order to obtain the most satisfactory results. It is best to make the solution of the indicator so that 0.5 c. c. shall be used with every 100 c. c. of solution titrated. The amounts of indicator to be used per litre of solvent are given as follows by Sutton and Thomson :

PER LITRE OF SOLVENT.

Indicator.	Solvent.	STRENGTH.	
		According to Sutton.	According to Thomson.
Litmus.	Water.....	20 grms.	20 grms.
Cochineal	Alcohol, 25 per cent..	100 "	
Rosolic acid	" 50 "	2 "	2 "
Phenol phthalein..	" 50 "	1 "	0.5 "
Phenacetolin.....	" 50 "	2 "	2 "
Lakmoid	" 50 "		1.5 "
Methyl orange	Water	1 "	0.15 "
Congo red	Water		0.5 "

Test-papers may be made with these indicators which may be found useful in many cases. In making test papers it will be found that many of the materials are resinoid in character, and if used in too large quantity the test paper will not readily be wetted by the solution to be tested. Very sensitive test-papers can be made by saturating filter-paper with solutions of the color which have been made slightly ammoniacal. On drying, the ammonia evaporates with the water, leaving the color in the proper condition. Litmus-paper is often made by the aid of a little gelatin in the solution. Such paper, however, will usually redden when moistened with water.

Preparing the Test Solutions.—The acids or caustic alkalis with which the test solutions are prepared cannot be conveniently weighed out with the requisite accuracy, and hence must be obtained indirectly. Pure, dry sodium carbonate can be used on the one hand and pure crystallized oxalic acid on the other ($\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$). The former is generally preferred, as being more readily obtained in an absolutely pure state. The possible impurities of the latter are moisture, sulphuric acid, lime, and ammonia. For this purpose, it should be purified by sublimation at a gentle heat, dissolving in water, and recrystallization.

Half-normal Sulphuric Acid.—Dilute about 30 c. c. concentrated pure sulphuric acid to one litre (or in that proportion). If a diluted acid is taken, dilute to a specific gravity of about 1.035. Cool to 15° or 15.5° C. after mixing well. The acid solution should be first made up preferably too strong than too weak.

Heat some pure sodium carbonate in a platinum dish until it sinters together. Transfer while hot to a small tube or flask, and allow to cool out of contact with the air. When cool weigh out and dissolve in the proportion of 53 grams to the litre ($\text{N}/2$ soln.). Mix thoroughly and fill a burette with some of the solution. Fill another burette with the sulphuric-acid solution. Run 10 c. c. of

the soda solution into a small beaker, add 50 or 60 c. c. of water, then run in 10 c.c. of the sulphuric-acid solution, boil out carbon dioxide (unless methyl orange is used as indicator), add 0.5 c. c. of solution of an indicator (cochineal or lakmoid) and run in the soda solution drop by drop until the color shows that neutrality has been reached. Note the amount of soda solution used, run into the beaker 10 c. c. more of the acid, and repeat the addition of the soda to neutrality as before, boiling up the solution in the beaker at least once after the addition of the most of the soda solution necessary. Repeat this operation a third or fourth time, and average the results for 10 c. c. of the sulphuric-acid solution. The results will show, for instance, that 10 c. c. of the sulphuric acid will neutralize 12.3 c. c. of the soda solution. In other words, every 100 c. c. of the sulphuric-acid solution must be diluted to 123 c. c. to make it half normal. Measure the amount on hand, dilute in the necessary proportion, mix well, rinse the burette with a little of the solution, fill up and test to verify the correctness in the same manner as before, taking the precaution to boil out the most of the carbon dioxide set free by the reaction. The sulphuric-acid solution must be brought to the point that one or fifty c. c. will exactly neutralize one or fifty c. c. of the soda solution. Keep in a bottle provided with a close-fitting glass stopper.

Normal Potash Solution.—The ordinary sticks of pure potash supplied for laboratory use contain usually 65 to 80 per cent of pure KOH. Make a solution containing approximately 49 grms. of KOH per litre (preferably a little too strong). After mixing and cooling, fill a burette with the solution and test it against the N/2 sulphuric acid in the manner already described. Dilute as may be necessary, and test again, finally by this means bringing it to the point where it will exactly neutralize the N/2 sulphuric acid c. c. for c. c. It is best to use the same indicator as before. The boiling may be dispensed

with, as there is little or no CO_2 to be expelled. Keep the solution in a bottle which has been provided with a tight-fitting *cork* which has been well soaked in melted paraffin.

The correctness of one of these solutions should be verified by at least one of the following methods:

1. Weigh out two or more grms. of dry pure sodium carbonate (such as was used for standardizing) in a platinum dish, run onto it a measured amount of the $\text{N}/2$ sulphuric acid (20 or 30 c.c.), avoiding any loss by effervescence, dry, ignite, and weigh. Every 100 grms. of the sodium carbonate entering into the reaction has thus been converted into 142 grms. of sodium sulphate, or, to express it differently, every 10 c. c. of $\text{N}/2$ sulphuric acid should have caused an increase of $\frac{1}{2} \left(\frac{142 - 106}{100} \right) = 0.180$ gm.

2. Determine the amount of sulphuric acid in 20 c. c. of the sulphuric acid by means of barium chloride.

3. Dissolve some pure crystallized oxalic acid in the proportion of 63 grms. per litre ($\text{N}/2$) and test the strength of the normal KOH solution. Solutions of oxalic acid of this strength may be kept some time; if more dilute they are liable to lose strength rapidly by decomposition of the acid.

Normal solutions of hydrochloric or nitric acids, and of caustic soda and ammonia, are preferred by some analysts. They may be prepared in the manner already described.

For some purposes $\text{N}/5$ or $\text{N}/10$ solutions are indispensable. They can be prepared directly or by careful dilutions of the stronger solutions by the aid of a well-graduated burette.

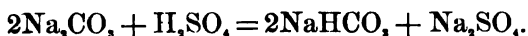
To avoid the errors incident to changes of volume in consequence of variations of temperature some analysts find it necessary to weigh instead of measuring their solutions. The solutions are made up essentially in the manner described, but one must finally determine the neutralizing power of one gram of the solution. For this

purpose flasks of various forms are used, the essential requirements being that they shall be of a size and capacity convenient for weighing in the balance-pan when partially or completely filled, that they shall be so closed as to prevent appreciable loss by evaporation, and that they shall be capable of delivering their contents in a stream or in small drops as may be necessary.

Uses of Alkalimetric and Acidimetric Solutions.—The total alkalimetry of caustic alkalies, their carbonates or bicarbonates, as well as that of caustic or carbonated alkaline earths, whether separate or mixed together, may be determined by means which readily suggest themselves. With carbonates the expulsion of CO₂ by heat after adding acid must never be omitted, since all the indicators are rendered less delicate by the presence of considerable quantities of that substance.

Caustic Alkali in Presence of Carbonate may be estimated in two or three ways. That of Thompson consists in adding to an excess of barium chloride to a solution of a known weight of the sample in the cold, and then, *without filtering*, titrating with N/2 sulphuric acid, using phenol phthalein as indicator. As barium carbonate is without effect on this indicator, the alkalinity remaining is due to the caustic alkali only. Filtering is dispensed with, since it is difficult to wash out all the alkali from the precipitated barium carbonate.

Alkaline Carbonate in Presence of Bicarbonate.—If the solution of the sample is made *very dilute*, and titrated *cold* with stirring, the tip of the burette being immersed in the solution, with phenol phthalein as indicator, the alkaline color is destroyed when *half* of the carbonate has been neutralized, the remainder having been converted into bicarbonate. The reaction would be of this type:



Sulphides of the Na₂S and NaHS type have effects

upon indicator similar to those of the carbonates and bicarbonates. For other methods see Sutton's Volumetric analysis.

Acids when combined with bases affording insoluble carbonates, when in soluble form may be estimated by precipitation by a measured quantity of sodium carbonate, and titration of the filtrate after filtering and washing. As a type of the reaction we may take the following:

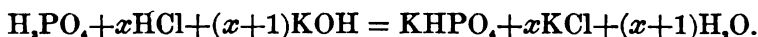
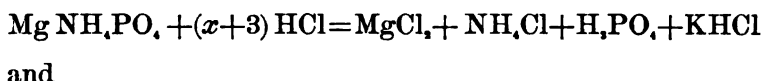


If the salt is neutral, the amount of sodium carbonate which has been neutralized is the measure of the acid present. Of course if several bases (precipitated by sodium carbonate) are combined with the same acid the estimation is equally possible. This method also will serve for the *estimation of bases* of that class even if combined with several different acids in a solution. The principle is applied in *Hehner's method* for the estimation of permanent hardness of waters.

Some Special Methods are sometimes used in certain cases. E.g., citric acid in soluble citrates is estimated by precipitation as the lead salt, suspending that salt in water, decomposing by H_2S , and after filtering off PbS , and boiling out H_2S , titration of the free acid. Oxalates of alkalies and alkaline earths can be converted into carbonates by ignition, and the alkalinity of the residue then determined. This plan is sometimes applied in examining other organic salts of alkalies and alkaline earths.

Phosphoric (and arsenic) acid may be estimated by a use of indicators. Alkaline di-hydrogen phosphates, e.g. $(\text{NaH}_2\text{PO}_4)$ are neutral to methyl orange and some others, while phosphates of the Na_2HPO_4 types are neutral to phenol phthalein. The different amounts of alkali found necessary to neutralize two equal portions of the same solution of phosphate, using methyl orange in one case and phenol phthalein in the other, will serve as a

basis for the calculation of the amount of phosphoric acid present. If the phosphoric acid precipitated as MgNH_4PO_4 , this precipitate may be washed free from ammonia by alcohol, dissolved in normal HCl or N/2 sulphuric acid, and the solution titrated back by normal alkali, using methyl orange as indicator. The reaction would be:



For every molecule of MgNH_4PO_4 ($= \frac{1}{2} \text{P}_2\text{O}_5$) two molecules of HCl have been neutralized, the equivalent of the third molecule having been neutralized in the back titration. (2d equation). Hence, 2 mol. HCl $= \frac{1}{2}$ mol. P_2O_5 , or 1 mol. HCl $= \frac{1}{4}$ mol. P_2O_5 , $142 \div 4 = 35.5$. The acid, being normal, 1 c. c. $= 0.0355 \text{ P}_2\text{O}_5$ in neutralizing power. By similar reasoning we would find that 1 c. c. $= 0.0575 \text{ As}_2\text{O}_3$ or 0.04 MgO . In applying this method it will usually be convenient to use N/10 solutions.

Alumina, Ferric Iron, and some other bases, when in neutral combination, afford salts neutral to methyl orange, congo red, etc. This fact is chiefly utilized in determining the proportion of free acid present in commercial salts of these bases. Atkinson (Chem. News, LII. 311) uses methyl orange for the determination of alumina in various compounds, by precipitation as hydrate, washing, suspending in water, adding the indicator, and titrating with normal acid. The end reaction is a little slow, and to assist in noting the change of tint he advises to have at hand, for comparison, a vessel of the same size and shape, containing the same bulk of water colored with the indicator.

CHAPTER XXXV.

COMMERCIAL BICARBONATE OF SODA.

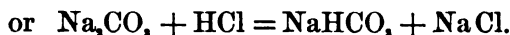


Soda.—Dissolve 1 gm. in about 100 c. c. of water, add methyl orange, and titrate with standard acid.

If desired the titration may be finished with tenth or twentieth normal acid. The methyl orange being practically indifferent to carbonic acid, the result shows "total alkalinity" or soda present combined both as mono- and as bi-carbonate.

Dissolve another gramme in 250 c. c. of cold water, add phenol phthalein, and titrate with tenth normal acid (or a weaker standard). The nose of the burette should dip into the solution, which should be well stirred during the titration.

Under suitable conditions of dilution and temperature the reaction is $2Na_2CO_3 + H_2SO_4 = 2NaHCO_3 + Na_2SO_4$,



No carbonic acid should escape from the liquid during titration, and 1 c. c. half-normal sulphuric or of full normal hydrochloric acid = 0.106 gm. Na_2CO_3 present, or *twice as much* as in the former titration with methyl-orange indicator.

In some works the amount of bicarbonate is determined by titration with caustic alkali, using the "spot" test (a drop on a white porcelain plate) with silver nitrate solution. The silver nitrate with mono- or bi-carbonate shows *white* silver carbonate. As soon, however, as all the bi-carbonate has been converted to mono-carbonate, the

least excess of caustic alkali shows a *dark brown* color. due to formation of silver oxide. The reaction is



and 1 c. c. normal caustic alkali = 0.084 gm. NaHCO_3 .

Water.—Weigh out 1 gm. in a platinum boat, and place the boat and contents in the centre of a piece of hard-glass tubing about 8 or 10 inches long. Connect the tubing at one end, by means of a tightly-fitting tube and cork, with a bottle containing concentrated sulphuric acid to dry the air drawn through it, and at the other end with a calcium-chloride tube, previously weighed and prepared, by passing CO_2 through it as previously described. (See Calcium Carbonate, page 36.) The point of the calcium chloride tube should be passed through the cork, as a connection of rubber tubing is very likely to condense the water driven off, which is drawn into the tube then only with difficulty. The other end of the calcium chloride tube is then connected with an aspirator. Start the aspirator, and then apply the heat of a Bunsen lamp to the tubing where the boat lies. Raise the heat steadily until the tube about it is red hot. Keep it at that temperature for fifteen minutes or more. Then withdraw the heat and allow it to cool, still keeping the aspirator at work, until the tubing and calcium chloride tube are cool. Weigh the calcium chloride tube. The increase in weight is the moisture present in the sample. Withdraw the boat, and weigh it with its contents. The loss represents water plus half the carbon dioxide. This should be one half the amount of the carbon dioxide as determined afterward.

Carbon Dioxide.—Introduce 0.5 gm. into the flask of a carbon dioxide apparatus, and 25 c. c. water containing 2 c. c. concentrated sulphuric acid, or 5 c. c. concentrated nitric acid, and determine the CO_2 as usual in carbonates, by absorption in a tube of soda-lime, etc. (See Calcium Carbonate, p. 35.)

Chloride.—Dissolve 1 gm. in 100 c. c. of water, just neutralize with HNO_3 , add a few drops of saturated solution of potassium chromate, (1 : 5) and titre with standard solution of silver nitrate. The silver nitrate solution is made by dissolving 17 gms. pure crystallized AgNO_3 in one litre of water. It is standardized by testing it upon a solution of pure fused sodium chloride* containing 1 gm. in 250 c. c. of water. The potassium chromate is used as an indicator, since the red silver chromate cannot form (permanently) until all of the chloride has been precipitated. The silver solution is, therefore, added until the liquid has a reddish tinge, which cannot be removed by vigorous stirring.

Sulphate.—Dissolve 3 or 4 gms. in water, acidulate slightly with hydrochloric acid, boil out the carbon dioxide, and determine SO_3 as usual with BaCl_2 .

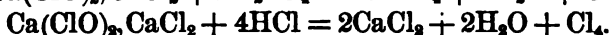
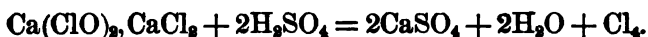
Calculation: Calculate the Cl to NaCl , the SO_3 to Na_2SO_4 . The Na_2O found by alkalimetric titration represents that combined as carbonate—mono or bi—since the neutral NaCl and Na_2SO_4 have no effect.

* Most conveniently prepared by neutralizing pure sodium carbonate with hydrochloric acid, evaporating to dryness and fusing. All ordinary salt (table salt) contains small amounts of sulphates, chiefly calcium and magnesium, and other impurities, which cannot be separated without some trouble.—E. W.

CHAPTER XXXVI.

CHLORIMETRY.

Bleaching powder, commercially known as chloride of lime, consists of a mixture, according to some a combination, of calcium hypochlorite, CaCl_2O_2 , and calcium chloride, CaCl_2 . Its value depends upon the amount of chlorine set free when an acid is added, known as "available chlorine," *e. g.* :



The available chlorine of bleaching powder is two atoms of Cl for each atom of O in the hypochlorite, or, as the formula indicates, O_2 and Cl_2 .

The compounds known commercially as chloride of soda (Labarraque's solution) and chloride of potash (Javelle water) are similar in composition (NaClO , NaCl) and (KClO , KCl), and are the same as regards the ratio of O and Cl.

"Iodized Starch" Paper.—Rub up in a mortar 3 gms. starch with 50 c. c. warm water, wash the creamy mixture into a beaker containing about 200 c. c. boiling water, stirring well until solution is effected. Now add a solution of 1 gm. KI and 1 gm. pure Na_2CO_3 , and dilute to half a litre. Moisten strips of filter-paper with this solution, and dry them for use, keeping them in a corked or stoppered bottle.

Arsenious Acid Solution.—Weigh out 4.95 gms. pure pulverized white arsenic (As_2O_3), transfer to a litre flask add about 25 gms. pure crystallized sodium carbonate, and 200 c. c. water. Boil gently, with frequent shaking until all is dissolved, cool, and dilute up to the litre

mark. One c. c. of this solution corresponds to 0.00355 available Cl, as may be seen from the following :



The four atoms of available chlorine in the bleaching powder correspond to the two atoms of O taken up by the As_2O_3 .

Molecular weight of $\text{As}_2\text{O}_3 = 198$

Molecular weight of $\text{Cl}_2 = 142$.

Since 1 c. c. of the arsenious solution contains

$$0.00495 \text{ gm. As}_2\text{O}_3 = \frac{4.950 \text{ gms. taken}}{1000 \text{ c. c. in 1 litre}}; \text{ then,}$$

$$198 : 142 = 0.00495 : 0.00355.$$

Analysis.—Weigh out 10 gms. of the bleaching powder, transfer to a mortar, add 50 or 60 c. c. of water, and rub to a cream. Allow the heavier particles to subside, decant the turbid supernatant fluid, add more water, rub up again, and continue thus until all the powder has been transferred to a litre flask. Fill the flask up to the mark, pour the contents into a beaker, mix it well, and take out 50 c. c. at a time for the analysis. The solution will always remain turbid, but this cannot be avoided, and does not interfere with the accuracy of the results, provided it is uniformly mixed. Into the 50 c. c. taken, run the arsenious solution, from a burette, until a drop of the solution taken out on a rod no longer produces a blue spot on the iodized starch paper, which has been previously moistened and spread out upon a white plate.

The calculation is readily made. Fifty c. c. of bleaching powder solution, made in the way described, is equivalent to 0.5 gm. Suppose this takes 45 c. c. of the arsenious solution. Since 1 c. c. arsenious sol. = 0.00355 gm. available Cl, 45 c. c. = $(45 \times 0.00355) = 0.15975$ gm. available Cl.

If then 0.5 gm. bleaching powder = 0.15976 gm. Cl,

1 gm. = 0.3195 gm.,

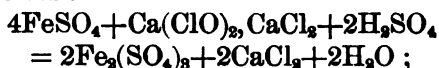
or the bleaching powder contains 31.95 per cent of available chlorine.

CHLORIMETRY (IRON METHOD).

Weigh out 10 gms. bleaching powder, place in a mortar, add 50 or 60 c. c. water, rub to a cream, allow the coarser particles to settle, pour off the turbid supernatant fluid into a litre flask, add more water, rub again, etc., until all the powder has been transferred to the flask, fill up to the mark, pour the solution into a beaker, and mix well; take out 50 c. c. for the analysis.

Weigh out in the mean time 0.325 gm. piano-forte wire (= 0.324 gm. Fe) and dissolve it in 2 c. c. conc. H_2SO_4 diluted with 10 c. c. water in a small valved flask. Cool, fill the flask with cold water, and pour into a large beaker. Now add 50 c. c. of the turbid bleaching powder solution, pouring it in slowly, stirring all the time. Dilute to about 500 c. c. Then, by means of a standardized solution of potassium permanganate (prepared as described under Ammonio Ferric Sulphate, p. 42), determine the amount of iron still remaining in the ferrous form.

The reaction is :



or four atoms Fe correspond to four atoms Cl, 56 parts Fe equivalent to 35.5 parts Cl.

The mode of calculating results is best shown by example.

Suppose 1 c. c. of the permanganate was equivalent to 0.003 gm. Fe, and that it took 23.8 c. c. of that solution to oxidize the ferrous iron not acted upon by the bleaching powder used, in an amount equivalent to 0.5 gm. 23.8 c. c. permanganate correspond to (23.8×0.003) or 0.0714 gm. Fe remaining unoxidized. Then 0.324 (Fe taken) — 0.0714 (Fe unoxidized) = 0.2566 gm. Fe oxidized by bleaching powder. Since 56 parts Fe correspond to 35.5 parts Cl, we have the proportion :

$$56 : 35.5 = 0.2566 : 0.1601 \text{ gm. available Cl.}$$

0.5 gm. bleaching powder contains 0.1601 available Cl

1 gm. contains 32.02,

or 32.02 per cent available Cl.

CHAPTER XXXVII.

FERTILIZERS.

Fertilizers are manufactured by mixing of various forms of refuse materials from other industries, where such refuse contains nitrogen or phosphoric acid or both, such as sugar-scums, refuse from slaughter-houses, fat-melting, glue-making, tanneries, leather-dressing etc. The principal source of the phosphoric acid is the phosphate rock from the Southern States, which, in pulverulent form, is mixed with suitable proportions of materials containing nitrogen, and then treated with strong sulphuric acid to render the most of the phosphoric acid "available," chiefly in the form of calcium superphosphate. Inevitably the finished fertilizers in the market contain more or less of what is called reduced (inverted, reverted, etc.) phosphate, which is not readily soluble in water alone, but dissolves in solutions of several organic salts, thus being, under some conditions, available for the purposes of fertilization of plant-crops.

For some purposes (tobacco culture, etc.) the addition of potassium salts to the fertilizer is necessary. These are usually added in the form of chloride or sulphate, which, under the name of Stassfurth salts, are largely imported for that purpose.

The methods here given necessarily include the examinations of material used in manufacturing fertilizers.

Moisture.—Inasmuch as the percentage of moisture in a fertilizer may vary considerably under the conditions to which it is exposed, a determination of moisture is always imperative, in order that the results on other con-

stituents as determined by different analysts, say those of the buyer and the seller, may be fairly compared.

Some analysts invariably heat to a certain temperature (100° to 110°C.) until a constant weight is obtained ; others heat for a certain time, 2, 3, or 5 hours, and call the loss moisture. The plan prescribed by the Association of Official Agricultural Chemists (vid. Bulletins of U. S. Department of Agriculture) is probably most uniformly followed. That is :

For alkaline salts, heat 1 to 5 gms. at 130° to constant weight.

For other material, heat 2 gms. (or 5 gms. if the sample be coarse) for 5 hours at 100° . The loss in either case is taken as representing moisture.

Phosphoric Acid.—The phraseology regarding the phosphoric acid in fertilizers is often confusing. As may have been inferred, three forms of phosphoric acid are recognized in fertilizers, viz :

1. That soluble readily in water, consisting presumably of calcium "superphosphate," $\text{CaH}_2(\text{PO}_4)_2$.

2. That not readily soluble in water, but soluble in certain organic solutions, presumably consisting of $\text{CaH}(\text{PO}_4)_2$ or acid ferric and aluminic phosphates.

3. That insoluble both in water and in the solvents for 2, remaining presumably in the condition in which it originally existed in the phosphate rock, $\text{Ca}_3(\text{PO}_4)_2$.

Notwithstanding the fact of there being numerous possible combinations between phosphoric acid and lime in a fertilizer, it is often required that a report shall show the amount of "bone-phosphate," $\text{Ca}_3(\text{PO}_4)_2$, to which any given percentage of phosphoric acid is equivalent. The percentage multiplied by 2.1831 will give the desired figure.

- 1 is called "soluble phosphoric acid" or "water soluble phosphoric acid."

- 2 has been called "reverted, inverted, reduced," etc., phosphoric acid, or, because it is usually determined by

washing it out with solution of ammonium citrate, it has been called "citrate soluble."

The sum of 1 and 2 is usually meant when term "available" phosphoric acid is employed. English analysts usually apply the term "available" as a synonym for "water soluble," and, on the other hand, the term "soluble" is also sometimes used when the sum of 1 and 2 is meant.

3 is usually called "insoluble," but to express it more exactly, it has also been called "citrate insoluble."

Much of this confusion of terms has arisen from the diversity of opinion as to the utility of these different forms in which the phosphoric acid may be combined.

The sum of 1, 2, and 3 is called "total phosphoric acid."

Total Phosphoric Acid.—The phosphoric acid is usually separated as the molybdate compound, which is dissolved in ammonia, and precipitated for weighing by magnesium mixture.

As the organic matter of the fertilizer would interfere with the complete separation of the phospho-molybdate, it must be destroyed (usually by ignition, with or without the addition of some nitrate). Hydrochloric acid is the best solvent for ignited phosphates, but the molybdate precipitation is best made in a nitric acid solution, so that, although after ignition hydrochloric acid must be used to effect solution, nitric acid and nitrates should largely predominate when the molybdate separation is effected.

Weigh out 2 gm. of the sample in a platinum dish, wet down with 5 c. c. of magnesium nitrate solution (600 gms. per litre), dry, and ignite. Ignition without addition of nitrate seldom induces any error, but is usually slower. After cooling, treat with 5 to 10 c. c. of hydrochloric acid, heat, then transfer to a beaker; add about 30 c. c. of nitric acid, boil and filter. When the fertilizers contain much iron and alumina more hydrochloric acid should be used. If made up with phosphatic slags, gelatinous silica will

appear, which requires evaporation to dryness, and taking up with hydrochloric acid.

A method recommended for fertilizers containing very large quantities of organic matter, consists in boiling with 20 to 30 c. c. of concentrated sulphuric acid in a Kjeldahl flask, adding crystals of sodium or potassium nitrate from time to time until the organic matter is destroyed, diluting, and filtering. The presence of much sulphuric or hydrochloric acid retards the separation of the molybdate precipitate, and is best avoided. Hydrochloric acid can be removed by evaporating low with excess of nitric acid; sulphuric acid, however, cannot.

In any case dilute the clear solution to 250 c. c., mix well, and take 50 c. c. for the analysis (representing 0.4 gm.).

With phosphate rock, etc., half this amount will suffice; add ammonia until it is just alkaline, then acidify decidedly by addition of 5 c. c. of nitric acid; add 10 to 15 gms. of ammonium nitrate crystals, warm to 80° or 90° C., and add molybdate solution in the proportion of 50 c. c. for every 0.1 gm. of phosphoric acid assumed to be present. For ordinary fertilizers which contain less than 20 per cent. P_2O_5 , 50 c. c. will be ample. Let stand warm, with frequent stirring, until the precipitate settles readily when disturbed; wash by decantation with cold dilute solution of ammonium nitrate acidified with nitric acid, allowing as little as possible of the precipitate to get on to the filter. Dissolve the precipitate in ammonia, and precipitate by magnesium mixture, adding it slowly to the clear solution, which is vigorously stirred. Let stand cold, and handle the precipitate in the usual manner. (See Magnesium Sulphate, Hydrodisodic Phosphate; also Iron Ore, etc.)

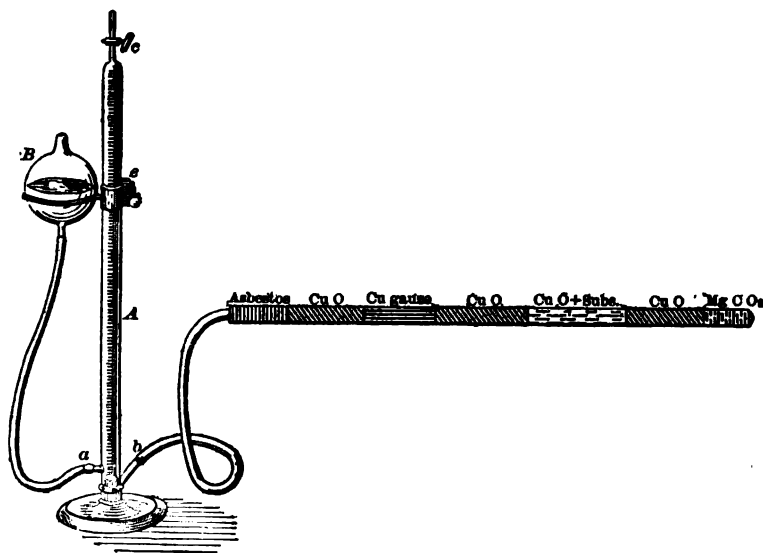
Water Soluble Phosphoric Acid.—Place 2 gms. of the well ground and mixed sample in a 9 cm. filter, and wash with successive portions of water (15 to 20 c. c. at a time), allowing each lot to run off before the next is added, until

the washings measure 250 c. c. If the washings contain but little organic matter, one fifth of the filtrate may be used for the molybdate precipitation in the manner above indicated, thus determining the water soluble phosphoric acid directly, or it may be determined indirectly by igniting the filter and contents and determining the phosphoric acid insoluble in water by the method prescribed for "total." In that case use the whole solution from the residue for the determination. The "water soluble" will then be found by difference.

"*Reduced,*" etc., or "*Citrate Soluble*" Phosphoric Acid.—Take 2 gms., wash out the "water soluble" as before, and then rinse the residue into a 200 c. c. flask by use of 100 c. c. of *absolutely neutral* ammonium citrate solution (of sp. gr. 1.09), cork the flask, immerse it in water at 65° C., and keep it at that temperature for exactly 30 minutes; then filter rapidly, and wash with water of about the same temperature. The "reduced" phosphoric acid is by this means removed. It will, however, be more convenient to determine it indirectly by igniting the filter-paper and contents, and carrying through the determination on the portion undissolved, which really constitutes the *Insoluble Phosphoric Acid*.

Ammonium tartrate, and also ammonium oxalate, have been used in place of the ammonium citrate, but the results with those salts have been found irregular and unsatisfactory, and their use has been practically abandoned. Especial care is necessary to have the citrate solution absolutely neutral—a result not attained by dissolving the ammonium citrate obtained from dealers in water. The Association of Official Agricultural Chemists prescribes: "Mix 370 gms. of commercial citric acid with 1500 c. c. of water; nearly neutralize with commercial ammonia; cool; add ammonia until exactly neutral (testing with saturated alcoholic solution of corallin), and bring to volume of 2 litres. Test the specific gravity, which should be 1.09° at 20° before using."

Nitrogen is found in fertilizers both in the form of ammonia (potential and actual) and as nitrate. By potential ammonia is meant the nitrogen which by process of decomposition of the organic matter of the fertilizer when in use will develop ammonia.



The "absolute" method for nitrogen consists in mixing the substance with copper oxide, and then heating to redness or above in a tube. The carbon and hydrogen take oxygen from the copper oxide and afford carbon dioxide and water, while the nitrogen is set free in the gaseous form. Copper oxide is introduced on both sides of the mixture of substance with the oxide in order to thoroughly burn up any volatile portions coming from the substance. In order to destroy any nitrogen oxides which may be present or be formed during the combustion, metallic copper (preferably in the form of a roll of wire gauze) is interposed in the path of the gases to the azotometer, the function of which is to abstract the oxygen from the nitrogen oxides under the conditions produced.

It has been often found that the copper gauze does more than is intended, and abstracts some oxygen from the carbon dioxide as well, giving small amounts of carbon monoxide; so to remedy this a third layer of copper oxide is interposed, which will reoxidize it to carbon dioxide.

To remove the air from the tube at the beginning of the operation, the extreme end of the tube is charged with coarsely crushed magnesium carbonate, which on heating evolves carbon dioxide, and sweeps the air from the tube before the combustion is actually begun. The magnesium carbonate is again heated at the close of the operation to drive the nitrogen remaining in the tube into the azotometer.

The azotometer (*A*) is a graduated tube, with stop-cock above and two side tubes below, at different heights. The lower part of the azotometer as well as the lower side tube is filled with mercury. The upper side tube and the remainder of the azotometer is filled (when ready for use) with strong solution of caustic alkali (to absorb carbon dioxide). The upper side tube is connected with a stop-cock bulb (*B*) containing the caustic alkali. The bulb is supported in such a way that it can be raised or lowered at will.

The copper oxide should be ignited and cooled before using. The portion which is to be mixed with the substance must be ground in a mortar until it is reduced to a fine sand.

Select a tube of good hard glass, seal one end in the flame, and cut to a length of 24 to 27 inches. Charge as follows:

Magnesium carbonate, crushed to pieces four or five times the size of a pin's head, $1\frac{1}{2}$ inches.

Coarse granular copper oxide, $1\frac{1}{2}$ to 2 inches.

Fine copper oxide mixed with the substance, 4 inches.
0.5 to 2 gms. of the substance are weighed out in a watch-glass, then mixed with the copper oxide, and poured into the tube by the aid of a small paper scoop or funnel. A

little more of the fine copper oxide is then used to rinse off the watch-glass, the whole amount being just about sufficient to fill the tube loosely without shaking down to the depth of about 4 inches.

Coarse granular copper oxide, about 8 inches.

Metallic copper, preferably in the form of a closely rolled coil of fine wire gauze, 3 inches.

Coarse granular copper oxide about 2 inches.

Asbestos Plug.

Lay the tube so charged in the trough of a combustion furnace and fit tightly to the open end a cork carrying a glass tube connected by means of a rubber tube with another tube dipping into the mercury in the azotometer.

The end carrying the cork should project from the furnace far enough to avoid charring the cork.

Then heat up the magnesium carbonate, starting cautiously at first so as not to break the tube. The air in the tube is thus driven into the azotometer. When the bubbles of gas rising through the mercury are completely absorbed by the caustic alkali in the upper part of the azotometer, heat up the copper oxide at the other end of the tube, using the same caution as before, carrying the heat slowly back until the metallic copper as well as a couple of inches of the copper oxide on each side of it is at a full red heat. Lower the heat on the magnesium carbonate, pinch the rubber connection between the combustion tube and azotometer for a moment, open the upper stop-cock of the azotometer, and by raising the bulb *B* force the gas (air, etc.), out of the azotometer. Close the azotometer stop-cock and release the connection. Then carry the heat slowly back to the mixture of the substance with the copper oxide, getting all of the tube except the magnesium carbonate end finally up to full red heat. The progress of the combustion may be judged by the rapidity with which the bubbles of gas pass through the mercury. It should not be faster than about two bubbles per second.

When they cease, heat up the magnesium carbonate

again, keeping up the heat until the gas driven from the tube is all absorbed by the caustic alkali. Then disconnect the azotometer, and cool down the tube. Allow the azotometer to stand for some time to cool completely, and hang near it a thermometer. Bring the bulb *B* close to the azotometer, and raise or lower it until the level of the solution in both is the same. Then read the volume of the gas and the temperature, and calculate the weight of the nitrogen.

When not in use the azotometer should be washed free from caustic alkali, especially as to the stop-cock, which should always be taken out, wiped off, and then freshly lubricated with a little vaseline.

The essential features of the *Kjeldahl process* are: 1. Digestion of the (more or less organic) material with boiling concentrated sulphuric acid, whereby it is eventually oxidized, the nitrogen present being converted into ammonium sulphate. 2. Distillation.

The acid is diluted, overneutralized with fixed alkali, and the ammonia distilled off. In the distillate any convenient method may be used for the estimation of the ammonia.

The process was originally devised by Kjeldahl of Copenhagen, for use in connection with the brewing industry (Fres., *Zts. Anal. Chem.*, XXII., 366).

In the first stage, Kjeldahl recommended to add cautiously small amounts of pulverized potassium permanganate toward the end in order to complete the oxidation. It seems best to avoid such addition where possible, and when it appears indispensable long heating had best be avoided after the addition.

To shorten the time of digestion, the addition of various substances has been proposed. Of those but two are now much used, viz., mercury (as metal or as oxide) and potassium sulphate.

Mercury compounds hasten the action very much. The addition of a small globule of the metal (equivalent to

about 0.7 gm. HgO) to each charge is the most efficient and convenient mode of applying it. The metal soon dissolves in the boiling acid, and exerts its effect. If the oxide is used, that prepared by precipitation from the chloride must be taken, since that prepared from the nitrate almost invariably contains nitrogen in some form which would or might affect the results. Whenever mercury has been used in the digestion some potassium sulphide must be used in the distillation in order to break up the mercur-ammonium compounds which would otherwise be formed.

The use of potassium sulphate in the digestion (Gunning, *Fres., Zts. Anal. Chem.*, XXIII., 188) tends to hold back the sulphuric acid, and to produce in a modified manner an oxidizing effect similar to that exerted in fusing with potassium bisulphate. The proportions recommended are one part of the sulphate to two of acid. (The U. S. Official Agricultural Chemists' Association recommended 10 gms. K_2SO_4 and 20 c. c. of concentrated H_2SO_4 .) The use of potassium permanganate to complete the oxidation is unnecessary.

Diluting for the purpose of neutralizing and distilling must be conducted with caution, or the flask may be fractured by the intense heat developed at the point of contact between the water and the acid mass (semi-solid when cold).

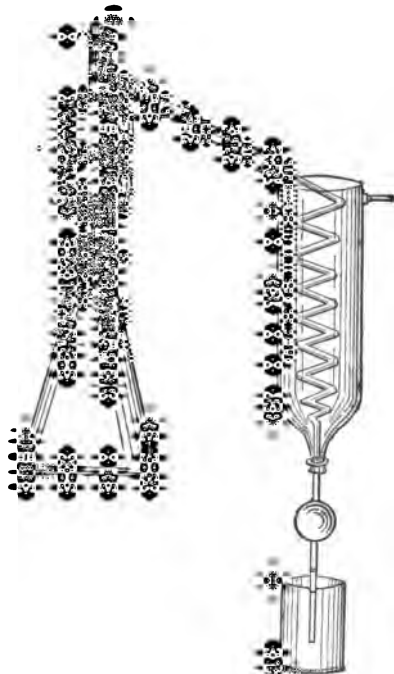
The nitrogen of nitrates affords little or no ammonia by the ordinary Kjeldahl process. The presence of organic matter tends to reduce some of the nitrate, and consequently afford some ammonia, but the major part usually escapes—sometimes practically all of it. To obtain the nitrogen of nitrates by the Kjeldahl process the plan followed resembles essentially the method of making aniline, viz., obtaining a nitro compound, and then converting this to an amine by nascent hydrogen.

Scovell's method is most used in the United States. The material is treated with concentrated sulphuric acid con-

30 c. c.). After mixing
 ed, little by little, and
 it shows no tendency
 d, whereupon a little
 e operation conducted

or each determination
 of nitrogen presumed
 izers 1 to 2 gms. are
 ch nitrogen a smaller

Special kind of glass and a



body, round bottom, with
 usually used (Kjeldahl
 most conveniently sup-

ported on a wire gauze in an inclined position. For distillation the pear-shaped flasks are not convenient, and the material had best be transferred to another flask, fitted with a two-bulb Wurz distilling tube. Some forms of flasks may be obtained in which the dilution, neutralization, and distillation may be effected without the necessity for transfer. The addition of a few pieces of freshly ignited pumice-stone to the solution before commencing the distillation will prevent bumping of the alkaline solution.

Of course the reagents should all be free from ammonia, and with untried reagents it is well to run through a blank test, using pure sugar.

The delivery-tube from the condenser should have attached a tube carrying a bulb, and the end of the tube beyond the bulb should dip below the surface of water, containing a measured quantity of standard acid (half normal to tenth normal according to requirements).

Potassium.—The Lindo-Gladding method is usually preferred. (See Potash Alum.)

Boil 10 gms. of the material with about 300 c. c. of water for 30 minutes. Then render just alkaline with ammonia, and add ammonium oxalate in quantity sufficient to precipitate all the lime present, cool, and make up to 500 c. c. and mix well. Filter and take off the filtrate lots of 25 c. c. or 50 c. c., according to requirements. Evaporate these down in platinum dishes after acidifying with sulphuric acid, finally igniting the residue until white. Dissolve in a little water, which should give a clear solution; acidify with a drop or two of hydrochloric acid; add 5 c. c. of platinum chloride, evaporate to a pasty condition; add 30 c. c. or more of strong alcohol (80 per cent or over), allow to stand cold for some time, and conduct the rest of the operation as already described (potash alum), washing with alcohol, then with ammonium chloride, then with alcohol (in a Gooch crucible), etc.

Regarding the examination of phosphatic materials to be used in the manufacture of fertilizers, a few suggestions may be desirable.

Spent bone-black, and other materials containing carbon or carbonaceous material as well as phosphate, may be ignited to burn off the organic substance, then dissolved in hydrochloric acid, and in general treated essentially as recommended for the determination of total phosphoric acid.

With phosphatic slags (Thomas slag) the first hydrochloric acid solution should be evaporated to dryness in order to remove the silica (which would otherwise appear in gelatinous form). Before proceeding with phosphate rock the proportion of iron and alumina oxides is of much importance on account of their tendency to afford the so-called "reduced phosphate" in the finished product. Glaser's method (*Zts. f. Angew. Chem.*, 1889, p. 636), or modifications thereof, has met with favor. It consists in dissolving the sample in aqua regia, adding sulphuric acid, and then a large excess of alcohol, which precipitates the calcium as sulphate. In the clear alcoholic solution the iron and alumina (as phosphates) may be determined.

A plan affording good results when carefully conducted would be as follows: Dissolve 2.5 gms. of the material in 10 c. c. of hydrochloric acid and 1 or 2 c. c. of nitric acid. Then add 10 c. c. of concentrated sulphuric acid, mix in well, and add strong alcohol (90 per cent or over) in sufficient quantity to bring the bulk of the solution, when well mixed and cold, up to 250 c. c. Shake well, and allow to settle for 30 to 60 minutes. Then filter off rapidly 200 c. c. (representing 2 gms.), neutralize very exactly with ammonia, boil out the alcohol, avoiding evaporation to dryness, and then render alkaline with a little ammonia, boil and filter. The precipitate, consisting of iron and alumina phosphate, is ignited and weighed by some, and half its weight taken as that of the iron aluminum oxide, which, roughly speaking, is true. It is, however, more exact and satisfactory to dissolve the moist hydrates in nitric acid, neutralize closely, precipitate out

phosphoric acid with a sufficient but not too large excess of ammonium molybdate, letting it stand warm for some hours, and in the filtrate precipitate with ammonia, boiling out the excess to render the alumina insoluble. Filter, and then treat the precipitate with about 10 c. c. of strong ammonia to dissolve out molybdic acid, wash again, and dry, ignite, and weigh the mixed oxides.

If desired, the precipitate may be brought into solution, and the iron reduced and titrated in the usual manner, the alumina being obtained by difference.

For fluorine determination in phosphate rock, see Calcium Fluoride.

CHAPTER XXXVIII.

COAL.

The sample should be carefully sampled and a fair average portion pulverized so that it will pass through a 40-mesh sieve.

Moisture.—Weigh out 1 to 2 gms. of the coal in a small shallow platinum dish, dry in an air-bath at 110° C. for half an hour, cool, and weigh, dry again in the bath for 15 minutes, cool, and weigh again.

Repeat this until the weight remains stationary or begins to increase. With many coals, especially those which are bituminous, the weight will often increase, no doubt as a result of incipient oxidation, probably before all moisture has been expelled.

It is usual, however, to take the lowest weight as that of the dried coal, and from the loss to calculate what is regarded as the moisture of the sample.

This portion may then be ignited, and the weight of the ash determined. In igniting to ash time may often be saved by removing the flame occasionally and allowing the mass to cool down, by which means air is drawn into the interstices. Then on applying the heat again more of the carbon is burned off.

When *cooled down* in these intervals the operation may also be assisted by stirring with a platinum wire, but caution must be exercised not to allow any of the light ash to be carried away by currents of air. Partially covering the dish with a strip of platinum foil while applying the heat may also prove of service.

Volatile Combustible Matter.—Weigh out 1 to 1½ gms. of the pulverized coal in a crucible provided with a lid

fitting closely enough not to permit ingress of air to any great extent. Apply at once the full heat of a good Bunsen burner. Keep this heat up for three minutes by the watch; then apply the heat of a blast-lamp for three minutes more, keeping the lid on throughout. Cool and weigh. The loss is moisture and volatile combustible matter. On deducting the moisture, found as already described, the remainder is volatile combustible matter. A small amount of soot may sometimes remain on the under side of the cover, and near the top of the crucible on the inside. This may be wiped off or burned off by careful management of the burner, but usually it weighs so little that it makes no important difference.

Fixed Carbon.—Lay the crucible on its side on the platinum triangle, support the lid so that it partially covers the mouth, and ignite over the burner until nothing but ash is left. The devices previously mentioned may be also used to burn off the carbon. The loss is designated as fixed carbon, and on deducting the weight of the crucible the *ash* is obtained.

Sulphur.—Eschka's method (*Oesterr. Zts.*, XXII., 111; *Ch. News*, XXI., 261) is now most generally used. Weigh out 1 to 1½ gms. of the pulverized coal in a shallow platinum dish. On top of this weigh out also 1 gm. of light magnesium oxide and 0.5 gm. of dry sodium carbonate. Mix the contents of the dish thoroughly by the aid of a stout platinum wire. Then heat the mass gradually to redness, stirring frequently until all the carbon has been burned off. If one is dealing with a red-ash coal, the mass eventually shows a reddish tint.

When all carbon has been apparently burned off, cool, and stir in about 1 gm. of coarsely pulverized ammonium nitrate crystals. Cover the dish, and heat to ignition to complete the oxidation. Cool, extract by boiling up with two or three successive lots of water (30 to 40 c. c. each time), acidify the solution with hydrochloric acid, bring to a boil, and precipitate the sulphur (now in the form of

sulphate) with barium chloride solution (see Magnesium Sulphate).

The sulphur may exist in the coal in three different forms—as organic sulphide, as mineral sulphide (usually iron pyrites), or as sulphate. Methods have been devised by which it is intended to distinguish between these forms, but as yet this view of the question has received but little attention from the users of fuel. It is customary to assume that all the sulphur found in a coal exists therein as iron pyrites, which is probably correct in many cases. Inasmuch as FeS_2 , on heating out of contact with the air is converted to FeS , the other molecule of sulphur being volatilized, it is the practice of some analysts to deduct one-half of the sulphur found from the “volatile combustible,” and the other half from the “fixed carbon;” but this plan is not so generally pursued as formerly. It is asserted that the sulphate found in the ash existed originally in the coal as sulphate, and also that in that form when in the coal it is as inert as silica or any other of the mineral constituents as regards attacking grate-bars, affording sulphurous acid among the products of combustion, etc. The subject has not thus far attracted the attention of users of coal.

Weight of a Given Volume of the Coal (1 cubic yard).—By weighing a fragment of the coal suspended from the balance by a hair in air and then in water the specific gravity may be obtained. The weight of a cubic yard may then be calculated; *e. g.* : Suppose the specific gravity to be 1.3488.

Now, 1 cubic foot of water weighs 62.355 lbs. (*Watts's Dict.*, V., p. 1010), and 1 cubic yard weighs $62.355 \times 27 = 1683.585$ lbs. \therefore 1 cubic yard coal weighs $1683.585 \times 1.3488 = 2270.819$ lbs., or, leaving off the decimals, 2271 lbs. The weight of 1 cubic foot of water may be regarded as $62\frac{1}{2}$ lbs.

Heating Power.—The practical question of how much steam can be made by the combustion of a known weight

of fuel is often of importance. At one time the method of determining this consisted in estimating the weight of metallic lead reduced from litharge on heating in a crucible with a known weight of the coal. This method was imperfect in practice, and moreover was found to be based upon erroneous premises.

The Lewis-Thompson calorimeter, notwithstanding some defects, is much used for this purpose on account of its simplicity of manipulation, and when carefully managed it affords results which are fairly satisfactory. The principles upon which it is constructed and operated are as follows: The object aimed at is to determine the number of pounds of water convertible into steam by the combustion of one pound of the coal.

The latent heat of steam is 967 calories—that is, the absolute quantity of heat sufficient to raise the temperature of 967 lbs. of water through one degree Fahrenheit will just suffice to convert one pound of water at 212° into steam at 212°. If, then, we should burn completely one pound of the fuel in such a way that the heat of the combustion is all transferred to 967 lbs. of water, the rise in temperature of the water in degrees Fahrenheit would give directly the number of pounds of water which can be evaporated by the combustion of one pound of the fuel. In practice, of course, the full amount of heat which is utilized is much less, but the test serves to compare one fuel with another.

It is evident that so long as the relative weights of fuel and water are the same, the same result will be attained: the instrument accordingly is constructed for the use of more convenient amounts—2 gms. of fuel and 1934 grammes (c. c.) of water. It must be noted that this construction is adjusted for the British Thermal Units (B. T. U.), although the French weights and measures are used. The British Thermal Unit or *caloric* is the amount of heat required to raise the temperature of one pound of water from 39° to 40° Fahr. The French unit or *calorie* is nearly

Amount of heat required to
 raise one of water from 4° to
 similarity of names for

only of a bell of sheet
 the coal is burned. The

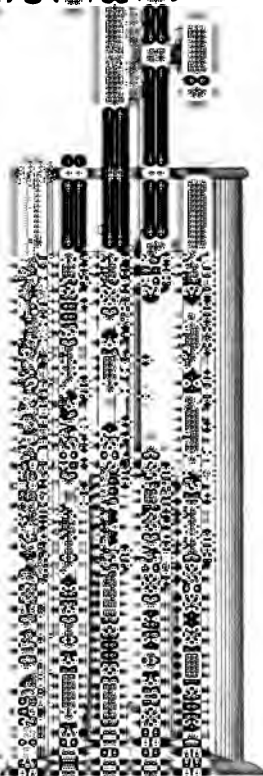


Fig. 1. CALORIMETER.

through holes near the
 through the water, im-
 the close of the opera-
 chamber that it may
 parts which were more
 burning fuel. The glass

vessel containing the water in which the copper vessel is submerged during the combustion is marked at 1934 c. c., that the right amount of water may be measured out for the test.

As a coal will develop the same amount of heat whether burned in air or in oxygen, the fuel is mixed with material which will supply oxygen. Potassium chlorate evolves some heat on parting with its oxygen; potassium nitrate, on the other hand, absorbs heat under those conditions. The mixture is therefore made with the two in such proportions that they will, as nearly as may be, neutralize one another in this respect, and practically be without influence upon the test. The proportions prescribed are 3 parts of chlorate to 1 part of nitrate. Of this mixture 8 to 12 times the weight of the coal is taken (22 grammes of the mixture to 2 grammes of the coal is the proportion most frequently used). All three—the chlorate, nitrate, and coal—should be pulverized separately until they will pass through a bolting-cloth sieve, and are then weighed out and thoroughly mixed. Especial care is necessary to insure the absolute dryness of the mixture of potassium salts. After mixture the material is placed in one of the copper tubes (“furnaces”), and gently pressed down. Tapping to settle it down is unadvisable. A half-inch length of fuse is then placed on the top. The fuse is made from loosely-twisted cotton wicking (such as is used in alcohol lamps), which has been soaked in solution of lead nitrate, and then dried.

The water cylinder should be filled to the mark with water somewhat cooler than the temperature of the room. As the rise of temperature to be expected is 12° to 15° Fahr., the water should be 7° or 8° below that of the room.

When everything is in readiness, the stop-cock closing the communication with the inside of the bell is shut, the charged “furnace” is placed in position in the clips of the base, the fuse is lighted, the bell placed over it, and the whole is quickly immersed in the water of the

glass cylinder before the combustion of the coal commences. During the combustion hold the bell in its place. When it ceases, open the stop-cock above so that water is admitted to the chamber, and move the apparatus up and down in the water a few times to establish a uniform temperature in the water. Insert a delicate thermometer in the water, and take the reading at the highest point attained. To allow for inevitable losses by radiation, absorption by the apparatus, etc., the rise in temperature is increased by ten per cent of its amount, a proportion found by experiment to give more nearly the correct result.

CHAPTER XXXIX.

COMMERCIAL NITRATES.

Several different methods are in use which require mention. The methods may be grouped as follows:

“*Refraction test*” or indirect determination; in which the impurities are more or less completely determined, and the remainder is regarded as nitrate.

Decomposition; in which the nitric acid is expelled by heating with some other acid (HCl , SiO_2) and the resulting combination weighed.

Oxidation methods; in which the oxidizing power of the nitric acid is brought into play, and either the oxidizing power is measured, or the nitric oxide gas resulting from the reaction is measured. (Ferrous salt tests, nitrometer.)

Reduction methods; in which the nitrogen of the sample is reduced to the form of ammonia, and then estimated.

The so-called “refraction test” is still frequently used in commercial work, though the results are often wide of the truth. The determinations made are: *Moisture, insoluble matter, chlorine, sulphuric anhydride, lime, and magnesia*. Some analysts also determine the potassium in some cases, and sometimes other tests are applied.

20 to 25 gms. of the sample are weighed out in a platinum dish, and the mass is slowly and carefully heated up to *incipient* fusion. On cooling and weighing the loss is taken as *moisture*. The material is then dissolved in water and filtered through a weighed filter to obtain *insoluble matter*. The solution and washings are made up to

some definite volume (500 c. c.) and aliquot portions taken for the different determinations: *e. g.*, 100 c. c. are titrated with *centinormal* silver solution for *chlorine*; 100 c. c. are taken for *lime* and *magnesia*—precipitated by ammonium oxalate, followed by hydrodisodic phosphate, etc.; 250 c. c. are taken for sulphuric anhydride determination by acidifying with hydrochloric acid, and precipitation with barium chloride.

In the presence of the nitrate the precipitate will always contain perceptible amounts of barium nitrate. Let settle, decant off closely through a filter, and then purify the precipitate by boiling it for 10 or 15 minutes with about 10 c. c. of strong solution of copper acetate containing free acetic acid.

The copper acetate solution should of course be free from sulphate or any substance precipitable by barium salts. Filter and wash, using enough acetic acid to prevent any contamination of the precipitate with basic copper salt. A somewhat longer mode of working consists in repeatedly evaporating the solution of nitrate nearly to dryness with excess of hydrochloric acid to convert all to chloride before precipitating with barium chloride.

Then calculate lime to CaSO_4 , and reckon the surplus SO_4 to soda or potash according as the sample is sodium or potassium nitrate. Calculate magnesium to MgCl_2 , and the remainder of the chlorine invariably to NaCl . The remainder is called pure nitrate.

In potash nitre the proportion of sodium nitrate is sometimes approximately estimated by ascertaining the amount of moisture taken up by exposing the salt to a moist atmosphere under a bell-jar for 14 days. Thorpe (*Quant. Chem. Anal.*, 9th ed., 1891; Wiley, N. Y.), p. 168, gives the following figures for 100 gms. of mixtures of potassium and sodium nitrates:

Per cent of NaNO_3	0.5	1	3	5	10
Gain in gms. in 14 days..	2.5	4	10	12	19

Potassium nitrate practically does not change in weight under these conditions.

Decomposition.—One method consists in treating a weighed quantity of the salt with excess of hydrochloric acid, evaporating to dryness, and repeating this two or three times to convert to chloride, finally drying and weighing. From the loss in weight is reckoned the amount of nitrate present. KNO_3 (101 parts) becomes KCl (74.5 parts), or NaNO_3 (85 parts) becomes NaCl (58.5 parts).

The more usual method is to mix 0.5 to 1 gm. of the powdered sample with five or six times its weight of pulverized and freshly ignited silica (or clean sand), and to ignite at a low-red heat for at least half an hour. Under these conditions the loss (allowing for moisture) is N_2O_5 . From this the percentage of nitrate may be calculated.

Oxidation.—The methods depending upon the oxidation of a known amount (excess) of ferrous sulphate or chloride, and titration of the ferrous iron remaining, require only a passing mention. (*Vid.* Pelouze, *Jour. Prakt. Chem.*, XL., 324; Bailhache, *C. Rend.*, CVIII., 1122, etc.) The reaction is: $6\text{FeCl}_2 + 2\text{NaNO}_3 + 8\text{HCl} = 3\text{Fe}_2\text{Cl}_6 + 2\text{NaCl} + 2\text{NO} + 4\text{H}_2\text{O}$. Methods depending upon the measurement of the nitric oxide gas evolved by the above or similar reactions are preferred.

Dr. Paul Wagner (*Chem. Ztg.*, VII., 1710) thus describes the method used by him: "In a flask of about 200 c. c. capacity are placed 40 c. c. of ferrous chloride solution containing 200 gms. of iron per litre. (It is advisable to keep a large stock of this solution at hand.) The flask is closed with a doubly perforated rubber stopper carrying two tubes; a gas delivery-tube delivering under water, and a stop-cock funnel-tube, the constricted end of which reaches into the body of the flask (not dipping into the ferrous chloride solution). The air is first boiled out of the flask, then 10 c. c. of a 'normal solution' con-

taining exactly 33 gms. of pure sodium nitrate per litre is poured into the funnel tube and the stop-cock is set so that the 'normal solution' drips slowly into the iron solution, which is kept boiling gently."

The nitric oxide gas evolved is caught in a eudiometer of 100 c. c. capacity, filled with water. When the solution has nearly all run in, the funnel-tube is twice in succession filled with 20 per cent hydrochloric acid. When all of this has been run in the operation is over, the eudiometer is put aside, replaced by another, and into the funnel-tube is poured 10 c. c. of a solution of a saltpetre or of a fertilizer to be tested, which has such a degree of concentration that 50 to 90 c. c. of nitric oxide gas will be evolved from the 10 c. c. of solution. When the evolution is at an end, which is easily detected by the complete collapse of the bubbles of steam in the delivery-tube, and the funnel-tube has been twice rinsed down with hydrochloric acid, six or seven other tests may follow in the same manner without renewing the iron solution, and finally a control test may be made with 10 c. c. of "normal solution" of nitrate. The filled eudiometers are meanwhile placed in a wide cylinder filled with water at any desired temperature. Now read off the volumes obtained, by which the calculation may be made very simply without any necessity for correcting for temperature and pressure.

Suppose, for instance, the first and last tests on the "normal solution showed concordantly, or, on the average, 90 c. c. of NO gas, this 90 c. c. then corresponds to 0.33 gm. NaNO_3 , or 0.05435 gm. N, or 1 c. c. corresponds to $0.05435 \div 90 = 0.000604$ N, and every c. c. of nitric oxide from the other determinations (since the conditions have been and are precisely similar) also corresponds to 0.000604 N; so that if, for example, in one of the tests 80 c. c. have been afforded, $80 \times 0.000604 = 0.04832$ gm. N is contained in the 10 c. c. of solution of that sample."

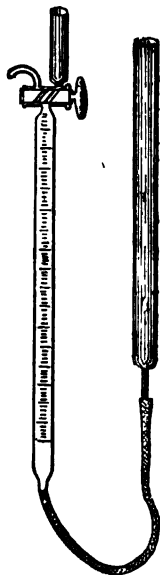
It may be suggested that the eudiometers when read off had best be raised by means of a test-tube holder until the

level of the water within and without is the same. Steadying by the hand is inadmissible, as it will warm the gas within and cause erroneous readings.

The *nitrometer*, as conceived by Crum and modified by Lunge, depends essentially upon the same principle. In this the nitric acid is freed from its combination by sulphuric acid, and reacts upon the mercury in the apparatus, the nitric oxide being measured as before. The reaction is:



For the analysis the equivalent of about 0.2 gm. of nitrate should be used for each test, dissolved in as little water as may be found convenient. With fairly pure nitrates a solution of 10 gms. of the sample in 250 c. c. of water, of which 5 c. c. is used for a test, would be a good proportion. This is likely to afford something less than 50 c. c. of gas. The graduated tube of the apparatus is lowered until its top is nearly even with the bottom of the ungraduated tube, and the mercury completely fills it, the stop-cock being open. Then 5 c. c. of the nitrate solution to be tested are poured into the cup, and the ungraduated tube is slowly lowered until the liquid has just been drawn in. The stop-cock is then closed, and 2 or 3 c. c. of concentrated sulphuric acid placed in the cup. Then lower the tube further, and after that cautiously open the stop-cock to let in the sulphuric acid. Before the last drops of acid have run in shut the stop-cock, and rinse out the cup with 2 or 3 c. c. more of sulphuric acid. Use a third installment in the same manner. As soon as the sulphuric acid mingles with the nitrate solution the reaction begins, and gas is generated as well as heat, so that it will require



a more decided lowering of the ungraduated tube to draw the sulphuric acid into the tube.

After the charge and rinsings are all in the tube should be tipped over two or three times to a position nearly horizontal, and then back to the vertical in order to mix the solutions. Raising and lowering the graduated tube will also assist mixing. The apparatus is then set aside for the reaction to become complete, and that the gas may take the temperature of the room. Then adjust the position of the tubes with respect to one another, so that the confined gas is presumably under the ordinary atmospheric pressure.

It may be assumed that every 6 or 7 mm. of the sulphuric solution is equivalent to 1 mm. of mercury, so that if the sulphuric acid solution occupies 13 or 14 divisions the mercury in the open tube should be two divisions above that in the graduated tube.

Put some concentrated sulphuric acid in the cup, and by cautious manipulation of the stop-cock determine the exact relative positions of the tubes to give a reading under the ordinary atmospheric pressure. For fine work read the barometer and thermometer, and calculate the volume of the gas at 0° C. and 760 mm. barometer, and from that the weight (1 c.c. of NO gas at the standard temperature and pressure weighs 0.001343 gm.), equivalent to

	0.002417 N ₂ O,,
	0.004521 KNO ₃ ,,
or	0.003805 NaNO ₂ ..

For much of this work the correction for temperature only will be necessary.

If a second nitrometer is at one's disposal, the manipulations may be performed with a known weight of pure material, and a comparison of the volumes obtained under precisely the same conditions will permit one to dispense with corrections for temperature and pressure.

For reduction tests the plan pursued is similar to that described for the determination of nitrates in water by means of the zinc-copper couple (*vid.* Fresh Water, Chap. XXXII). The amount of ammonia obtained from a fair amount of the sample is, however, so much larger that it must be distilled off into standard acid and determined alkalimetrically.

The reaction depends upon the fact that *nascent* hydrogen reduces the nitrogen of a nitrate to ammonia.

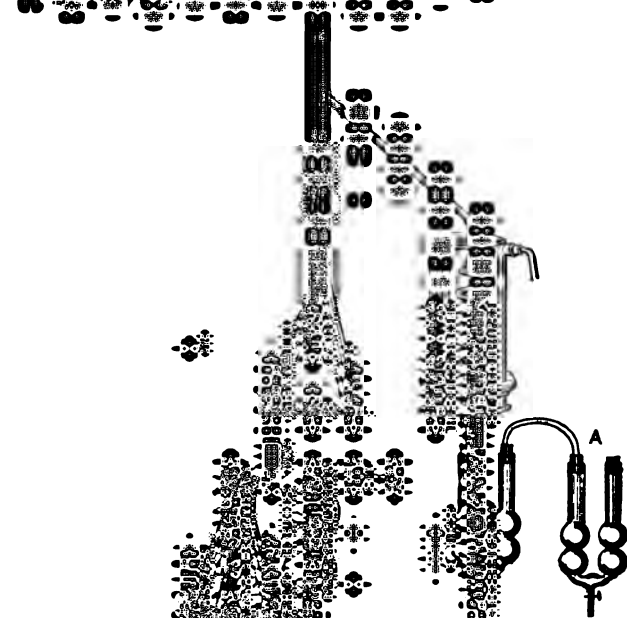
Zinc, which may be dissolved in either acid or alkaline solutions with evolution of hydrogen, is chiefly used in these methods, either alone or conjoined with copper or with iron filing. Aluminum or magnesium may also be used, and one or the other may be preferred. The solution for use is preferably a strongly alkaline one. The degree of dilution of the sample varies with different analysts. The proportions recommended vary from 1 part of nitrogen in 5000 of water (equivalent to about 1 gm. KNO_3 in 700 c. c.) to 1 gm. of nitrate in 20 c. c. 1 gm. of the sample in 100 c. c. of water is a convenient proportion. The arrangement of the apparatus is also very varied.

The principal points requiring attention are that the reaction shall occur in an enclosed flask or retort, from which the gases containing the ammonia generated can only escape through standard acid which is to be titrated afterward. The vessel in which the reaction occurs must be capable of being heated to the boiling temperature to drive out the ammonia formed. Rubber corks, or lengths of rubber tubing, in the connections are best avoided. Instead of rubber corks it is better to use ordinary corks soaked in paraffine.

One arrangement which will serve the purpose is suggested by the sketch. It consists of an Erlenmeyer flask, surmounted by a Wurtz tube, the side neck of which is connected with a condenser. The ends of the tubes should abut sharply against one another, with about half an inch of rubber tubing over the joint to hold them in place.

ATES.

passes through a cork (stop-cock) connected tubes are to be charged with dilute sulphuric acid (1 part of acid to 10 parts of water), if necessary, to form



albed flask, B, may be charged with 50 to 70 grammes of water and 25 gms. of iron filings, and 10 to 100 c. c. of water. To this add about 20 c. c. of dilute sulphuric acid and allow the whole to stand for 24 hours. Then apply heat to the flask; when the liquid begins to boil, stop the heating, and keep this up for 24 hours. The liquid is then distilled over. The residue is rinsed into a beaker; the liquid is then added, and the solution is finished with tenth

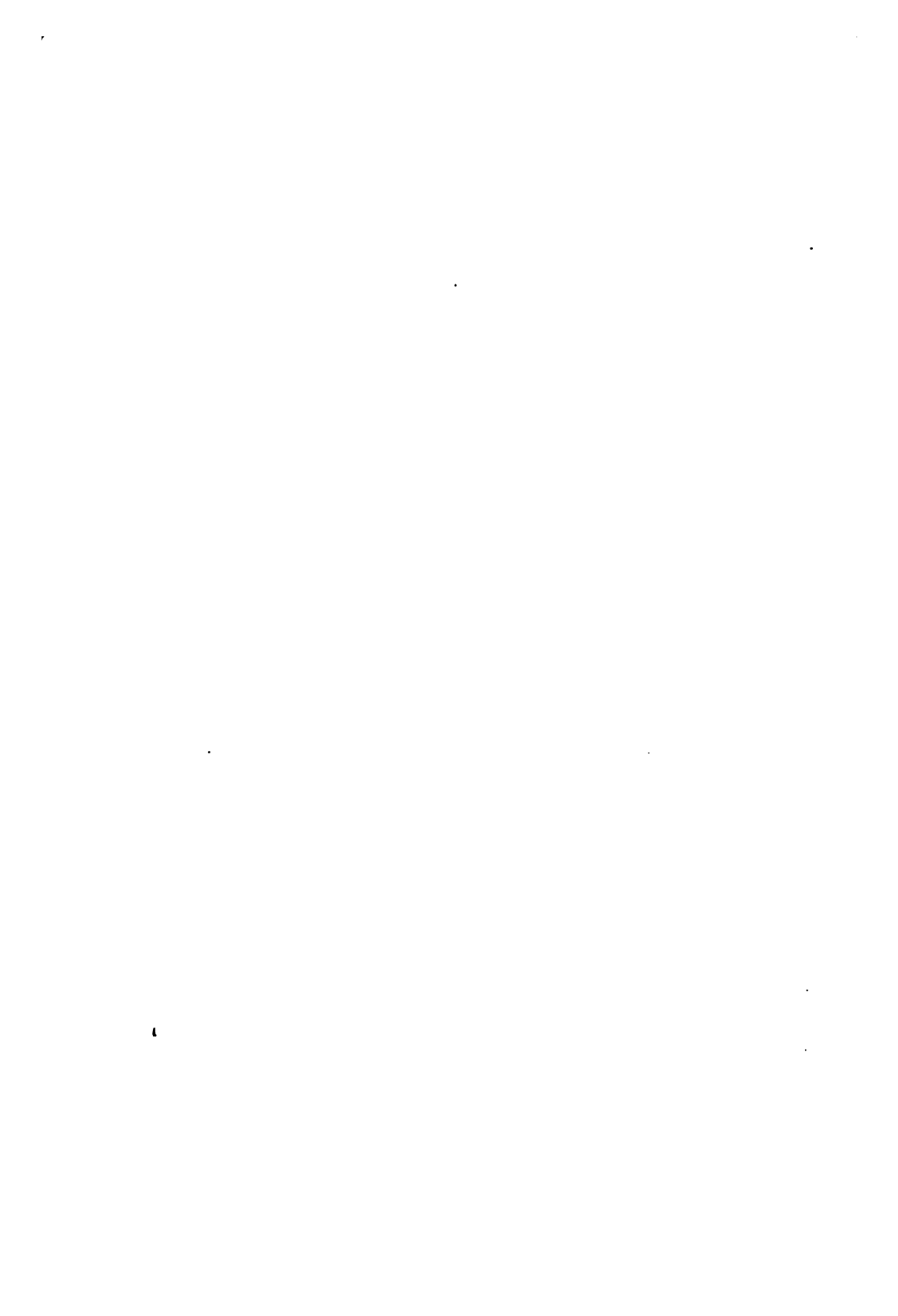
normal. 0.5 gm. of pure potassium nitrate will afford, roughly speaking, enough ammonia to neutralize 5 c. c. of half-normal sulphuric acid, so that from the general appearance of the sample one can judge when to stop the addition of the stronger alkaline solution. The action with the indicator may also serve as a guide.

The calculation is easy. Suppose 0.5 of crude sodium nitrate (Chili saltpetre) had been taken, and 15 c. c. of half-normal acid; the back titration required 10 c. c. of full normal, and 8 c. c. of tenth-normal alkali: then $(15 - 10.8)$ 4.2 c. c. of the normal acid was neutralized by the ammonia from the sample. 1 c. c. normal acid = 0.014 gm. NH_3 , or = 0.085 gm. NaNO_3 (molec. wt. 85), and $4.2 \times 0.085 = 0.357$ gm. NaNO_3 in 0.5 gm. of the sample, or 71.4 per cent.

A blank test should be made with the reagents used to guard against errors, especially those which might be due to the presence of nitrogen in the metal used.

Many color methods for the determination of nitric acid have been devised, but as a rule they are not conveniently applied in the examination of commercial nitrates, but are better suited for the estimation of nitrates when comparatively small in amount, as in water analysis, etc.

APPENDIX



APPENDIX

PROPERTIES OF PRECIPITATES, ETC.

By E. WALLER, Ph.D.

One division of Fresenius' book on *Quantitative Analysis* treats of "Forms," in which are given the properties of the various forms in which substances are separated for the purpose of weighing and determination.

It has seemed to the writer that those properties might be described in a manner more convenient for reference, and also that there might be added the properties of various precipitates, etc., which are used in analytical work for purposes of *separation*. Of course, only those properties are considered which have a bearing on the usual manipulation of the different substances. For convenience the information has been grouped under the heads:

"*Remarks*" (*Rem.*), giving points not properly belonging under any of the succeeding heads.

Conditions (*Cond.*), referring to the character of the solutions in which the separation can be made.

Solubilities (*Sol.*), under which the influences of different solvents which may be used in ordinary work is considered.*

* The terms "soluble" and "insoluble," as used in text-books of analytical chemistry, are usually misunderstood by students. The terms are used in a relative—not in an absolute—sense; *e. g.*, when a precipitate is said to be "insoluble" the meaning usually is that under ordinary conditions of work, with a moderate bulk of solution, etc., the degree of solubility is so small that no material error is involved by regarding the separation as complete.

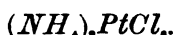
Contaminants (Contam.), which is restricted to those substances only which would not be expected to precipitate if alone under the conditions obtained.

Ignition (Ign.), or the behavior of the compounds designated on heating to a high heat in the way usually pursued with most of them. Under this head it is also necessary to consider the effect of ignition in contact with filter-paper or other carbonaceous substances indicated for brevity as "C."

A table is given which is intended to indicate at a glance the precipitates, etc., used and the forms in which they are weighed in case that is the object in view. Of

Element, etc.	Purpose.	Obtained or Precipitated as	Prepared for Weighing by	Weighed as
NH ₄	Weighing.	(NH ₄) ₂ PtCl ₆	{ Drying. Ignition.	(NH ₄) ₂ PtCl ₆ or Pt
K	"	K ₂ PtCl ₆	{ Drying or Ignition.	K ₂ PtCl ₆ or Pt
	"	KCl	"	KCl
	"	K ₂ SO ₄	"	K ₂ SO ₄
Na	"	NaCl	"	NaCl
	"	Na ₂ SO ₄	"	Na ₂ SO ₄
	"		"	CaSO ₄
Ca	"	CaC ₂ O ₄	{ " "	CaCO ₃ CaO
	Separation.	CuCO ₃		
Mg	Weighing.	MgNH ₄ PO ₄	"	Mg ₂ P ₂ O ₇
	Separation.	Mg(OH) ₂		
Ba	Weighing.	BaSO ₄	"	BaSO ₄
	Separation.	BaCO ₃		
Fe	Weighing.	Fe ₂ (OH) ₆	"	Fe ₂ O ₃
	Separation.	Fe(OH) ₃ (C ₂ H ₃ O ₂) ₃₋₄		
Al	Weighing.	Al ₂ (OH) ₆	"	Al ₂ O ₃
	"	Al ₂ (PO ₄) ₃	"	Al ₂ (PO ₄) ₃
	Separation.	Al ₂ (OH) ₆ (C ₂ H ₃ O ₂) ₃₋₄		
Cr	Weighing.	Cr ₂ (OH) ₆	"	Cr ₂ O ₃
Ti	"	H ₂ TiO ₃	"	TiO ₂
	Separation.	Na ₂ TiO ₃		
Zn	Weighing.	2ZnCO ₃ ·3Zn(OH) ₂	"	ZnO
	"	ZnNH ₄ PO ₄	{ " "	Zn ₂ P ₂ O ₇
	Separation.	ZnS·H ₂ O		ZnNH ₄ PO ₄
Mn	Weighing.	2MnCO ₃ ·H ₂ O	Ignition.	Mn ₂ O ₃
	"	MnNH ₄ PO ₄	"	Mn ₂ P ₂ O ₇
	Separation.	MnO ₂		

course, the forms designated as for *weighing* can also be used for purposes of *separation*.



Rem.—Precipitant, $PtCl_4$.

Yellow, perceptibly crystalline if formed slowly. Sometimes it is dissolved from the paper by hot water into a weighed capsule, and the solution evaporated, thus avoiding the uncertainties involved in the use of weighed filters.

Cond.—Solution should contain only chlorides. Sodium salts only permissible. Solution should be cold, slightly

Element, etc.	Purpose.	Obtained or Precipitated as	Prepared for Weighing by	Weighed as
Ni	Weighing.	Ni(Electro)	Drying.	Ni
	"	Ni(OH) ₂	} Ignition.	NiO
	"	Ni ₂ (OH) ₂		
	"	NiS.H ₂ O		
Co	Separation.	6KNO ₃ .Co ₂ (NO ₃) ₂	Ignition.	3K ₂ SO ₄ +2CoSO ₄
	Weighing.	CoS.H ₂ O		
Cu	Separation.	Cu(Electro)	Drying.	Cu
	Weighing.	Cu(OH) ₂	} Ignition.	CuO
	"	CuS		Cu ₂ S
	"	PbSO ₄	"	PbSO ₄
Pb	Weighing.	PbCrO ₄	Drying.	
	"	PbS		
	Separation.	AgCl	Ignition.	AgCl
Ag	Weighing.	As ₂ S ₃	} Drying.	As ₂ S ₃
As	"	MgNH ₄ AsO ₄		Mg ₂ As ₂ O ₇
	"	Sb ₂ S ₃	} Ignition.	Sb ₂ O ₃
	"			Sb ₂ S ₃
Sb	"		} Drying.	
	"			
Sn	"	H ₂ SnO ₃	} Ignition.	SnO ₂
	"	SnS ₂		
S.SO ₂ S ₂ O ₃	} Weighing	BaSO ₄	"	BaSO ₄
SO ₂ , etc.				
P, P ₂ O ₅ , etc.	Weighing.	MgNH ₄ PO ₄	"	Mg ₂ P ₂ O ₇
	Separation.	12MoO ₃ (NH ₄) ₂ PO ₄ +Na ₂ CO ₃ .K ₂ CO ₃ , etc.		
C, CO ₂ , etc.	} Weighing	or Na ₂ CO ₃ +CaCO ₃	} Absorption.	Na ₂ CO ₃ .K ₂ CO ₃ , etc.
		BaCO ₃		or Na ₂ CO ₃ +CaCO ₃
Si & SiO ₂	"	xH ₂ O SiO ₂	} Ignition.	BaSO ₄
Cl	"	AgCl		SiO ₂
N & HNO ₃	Measuring.	N or NO	"	AgCl
	Titration.	NH ₃		
	Weighing.	(NH ₄) ₂ PtCl ₆		(NH ₄)PtCl ₆ or Pt

acid, consisting chiefly of strong alcohol; an excess of PtCl_4 should be present.

Sol.—Somewhat soluble in cold, more so in hot, water. Fairly insoluble in strong alcohol, though more soluble than the corresponding potassium compound. Solubility in alcohol diminished by addition of ether. Its solubility also increases more rapidly by a rise in temperature or the dilution of the alcohol. Solubility increased by acid (HCl) or by alkali, diminished by PtCl_4 or Na_2PtCl_6 .

Contam.— NaCl which is not very soluble in alcohol. If sufficient PtCl_4 has been added to form Na_2PtCl_6 , the amount of contamination is small. The Na_2PtCl_6 crystals are more strongly colored and different in shape (needle-shaped) so that they can be readily detected. Can be removed by a short digestion with cold alcohol.

Ign.—Decomposed, leaving spongy platinum. Unless the heat is slowly raised some Pt may be volatilized with the products of decomposition.

KCl.

Rem.—Obtained by evaporation of the solution, and gentle ignition. Frequently, when in admixture with NaCl , the sum of the chlorides is thus obtained, and the KCl determined by PtCl_4 , the NaCl calculated, or the chlorine is determined and the proportions calculated. Salts containing K combined with acids capable of expulsion by HCl may be evaporated with excess of HCl .

Cond.—Solution should contain only chloride or salt convertible into chloride by evaporation with HCl . Ammonium salts and such others as may be expelled by evaporation and gentle ignition may be present.

Sol.—Soluble in water, less so in alcohol or strong HCl .

Contam.— NaCl , see under *Rem.* If the solution has been long exposed to the air of the laboratory, it usually contains some organic dust, which carbonizes by ignition, requiring filtering and re-evaporation.

Ign.—Decrepitates somewhat unless dried for some time.

Fuses at a low red heat, and volatilizes at temperatures a little higher, a small amount of caustic alkali being usually formed at the same time.

K₂SO₄.

Rem.—Obtained by evaporation of the solution, or by adding H₂SO₄ to solutions containing combinations with volatile acids (chloride, nitrate, acetate, etc.), evaporating and igniting. In cases of admixture with Na salts, processes similar to those indicated under KCl may be used.

Cond.—Salts forming non-volatile sulphates, or containing non-volatile acids (H₃PO₄, etc.), should be absent.

Sol.—Moderately soluble in water; much less so in alcohol.

Contam.—Na₂SO₄ or other non-volatile sulphates.

Ign.—Practically non-volatile in the heat of an ordinary Bunsen burner if the heat is not unnecessarily prolonged. Where the solution has contained an excess of H₂SO₄, some undecomposed KHSO₄ always remains, which can be best decomposed or converted into K₂SO₄ by heating with a few lumps of solid ammonium carbonate. Ignited with C, K₂S may be formed. The conditions usually obtained, however, do not afford this result.

K₂PtCl₆.

Rem.—Precipitant, PtCl₄.

More strongly colored than the corresponding ammonium salt, but otherwise resembling it in general characters. Like that compound, it is sometimes dissolved in hot water, and the solution evaporated in a weighed capsule, so as to dispense with weighed filters.

Cond.—Solution should be cold, alcoholic, and should contain preferably only sodium salts other than KCl. Chlorides or HCl should be present. Small amounts of Mg or Ca are permissible, though disadvantageous.

Sol.—Somewhat soluble in cold, more so in hot water. Insoluble in strong alcohol and in ammonium salts. Solu-

bility increased by acid or alkali, diminished by PtCl_4 or Na_2PtCl_6 .

Contam.— NaCl and other salts (as sulphates) not soluble in alcohol. Such contaminants are most readily removed by washing with aqueous solution of NH_4Cl , previously saturated with K_2PtCl_6 .

The NH_4Cl must afterward be removed by washing with alcohol.

If bromides are present, the precipitate may sometimes contain Br in place of Cl in the molecule.

Ign.—Alone, it is imperfectly converted to KCl and spongy platinum; with a reducing agent (as $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$), the conversion is complete. The heat should not be too rapidly raised. If ignited in platinum too high a heat may fuse the finely divided metal to the platinum vessel. After ignition, the KCl formed must be washed off with water before weighing.

Boiling the precipitate with formic acid (HCHO_2), or formic aldehyde (CH_2O), also reduces to metallic Pt —a method used by some analysts. This treatment often gives a finely divided “platinum black,” which may run through the filter-paper, or otherwise give difficulty in collecting for weighing.

NaCl.

Rem.—See *Rem.* under KCl .

Cond.—As for KCl .

Sol.—Soluble in water; much less so in strong HCl or alcohol. Less soluble in these menstrua than KCl .

Contam.— KCl (see KCl) or other non-volatile salts.

Ign.—Decrepitates violently on heating unless very thoroughly dried. Fusible at full red heat and volatilized at a temperature but little above its point of fusion. The temperatures of fusion and volatilization are, however, perceptibly higher than with KCl . Becomes slightly alkaline on fusion from loss of Cl .

Na₂SO₄.

Rem.—The suggestions as to K₂SO₄ throughout are applicable also to Na₂SO₄ (see K₂SO₄) even to the formation of NaHSO₄ by evaporation with excess of H₂SO₄ and ignition.

CaC₂O₄.

Rem.—Usual precipitant (NH₄)₂C₂O₄. Precipitated cold or in very dilute solutions, it separates in a very fine powder. In any case, boiling for a short time and then adding a few drops of ammonia is advisable before proceeding to filter. If precipitated in boiling alkaline solution, the solution bumps vigorously. Enough oxalate should be added to convert all Mg present into MgC₂O₄.

Cond.—Best precipitated in a boiling neutral solution, which should contain only Mg and alkalis besides the Ca.

Sol.—Dissolved by mineral acids, slightly soluble in acetic. Somewhat soluble in MgCl₂. Insoluble in MgC₂O₄. From its solutions in mineral acids, ammonium hydrate or other alkalis precipitate it unchanged.

Contam.—MgC₂O₄, which is removed by re-solution in HCl and reprecipitation by ammonium hydrate. If the proportion of Mg present is large this re-solution and reprecipitation may have to be repeated two or three times.

Ign.—Affords first CaCO₃, afterward CaO. Under ordinary circumstances the product is a mixture of the two. To obtain CaO it is necessary to ignite for some time over a blast-lamp. To obtain CaCO₃, it is ignited moderately, and repeatedly moistened with ammonium carbonate and gently ignited after each addition.

Ignited with H₂SO₄, it affords CaSO₄, which is frequently partially reduced to CaS by ignition with C, requiring further treatment with H₂SO₄ and ignition. The easiest mode of management is to transfer the filter-paper containing the precipitate still wet to an ordinary fusion crucible, and wet down with concentrated nitric and sulphuric acids. Then expel the excess of acid with a gentle heat, and finally ignite. A second treatment with H₂SO₄,

is often necessary. Instead of H_2SO_4 , a strong solution of $(\text{NH}_4)_2\text{SO}_4$ containing free ammonia and about 2 gms. NH_4Cl per 100 c. c., has been recommended (*vid.* Crooke's *Select Methods*, 3d ed., p. 46).

CaCO_3 .

Rem.—Usual precipitant $(\text{NH}_4)_2\text{CO}_3$. For separation or determination of CO_3 , the reagent is CaCl_2 with ammonium hydrate. Usually obtained for separation. At first it separates in flocculent or amorphous form, but after a short time assumes a crystalline form. This change is hastened by warming.

Cond.—Large proportions of alkaline salts, especially citrates, and of magnesium salts should be avoided. An alkaline solution is, of course, necessary.

Sol.—Soluble in water containing CO_2 ; very soluble in all acids; decomposed and dissolved by NH_4Cl , slowly in the cold, quickly if hot. Insoluble in water containing ammonium carbonate and ammonia.

Ign.—Converted to CaO as described under $\text{Ca}_3\text{C}_2\text{O}_6$. The change is more readily effected if some carbon is mixed with it.

MgNH_4PO_4 .

Rem.—Usual precipitant for $\text{Mg} = \text{Na}_2\text{HPO}_4$; for P_2O_5 (ortho) = "magnesia mixture," preferably that made with MgCl_2 .

Microcosmic salt ($\text{NaNH}_4\text{HPO}_4$) as a precipitant for Mg often gives a finely divided precipitate which runs through the pores of the filter.

Should be crystalline; if flocculent, some contaminant is present. When the proportion of precipitate which can form is small relatively to the bulk of the solution, some hours are necessary for complete separation.

Completeness of precipitation much accelerated by cold and agitation.

When washed as usual with diluted ammonia, alkaline

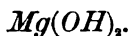
phosphate (Na_2HPO_4 , etc.) is not very rapidly removed, the salt being less soluble in ammonia than in water.

Cond.—Absence of silica or any bases other than alkalis. NH_4Cl or ammonium salts should be present.

Sol.—Solution should be cold for precipitation and filtration. Soluble in acids, even when weak, in hot solutions, and, to some extent, in cold water; insoluble in dilute ammonia.

Contam.—Silica and $\text{Mg}(\text{OH})_2$, or basic salts of Mg. The latter is only likely to occur when the precipitate is used for the purpose of determining P_2O_5 or P. The difficulty is avoided by adding the Mg mixture (preferably the chloride) slowly with stirring. Silica may be weighed and deducted after ignition, weighing and dissolving in acid. MoO_3 may also occur when the molybdate separation has preceded.

Ign.—Should be well dried before igniting. If heated too rapidly some loss may result from too rapid decomposition. If the filter-paper is allowed to burn with flame, some particles of the precipitate (in weighable amount) may be mechanically carried off. The precipitate has afterwards a tendency to sinter together at a moderately high heat, thereby preventing the oxygen of the air from penetrating the mass and oxidizing the carbon, the precipitate being left gray or black. The best mode of managing is to expose the precipitate for some time to a dull red after the carbonization of the paper, and, finally, finish with the full heat of the Bunsen burner. If the precipitate comes black, repeated moistening with nitric acid and cautious ignition is to be recommended.



Rem.—Usual precipitant $\text{Ba}(\text{OH})_2$, for separation from alkalies when these are to be determined.

Cond.—Alkaline solution moderately concentrated, containing no NH_4 salts.

Sol.—Dissolved by acids or ammonium salts. Precipi-

tation partly prevented by presence of organic salts, citrates, tartrates, sugar, etc.

Contam.—Usually unimportant, the object generally being to remove from the solution MgO and all substances except those readily separable by ammonium carbonate.

BaSO₄.

Rem.—Precipitant for SO₄—BaCl₂; for Ba = H₂SO₄.

Precipitated in an extremely fine state of division (runs through filter-paper) if formed in cold or dilute solutions, or such as contain ammonia salts. Forms slowly if small in amount.

The tendency of the precipitate to creep up the side of a beaker may be checked by adding a drop of HCl.

Cond.—Hot solution acidified with HCl. Hydrofluosilicic acid or silica should be absent, also large proportions of calcium salts, or salts of the (NH₄)₂S group of bases.

Sol.—Soluble in concentrated H₂SO₄, in HCl when moderately strong and hot, and in HNO₃ even when tolerably dilute. It is also soluble in hot Fe₂Cl₆, in alkaline and alkaline-earth nitrates, metaphosphates, citrates, and salts of some other organic acids.

Insoluble in water, in dilute HCl, and in acetic acid.

Contam.—The especial difficulty with BaSO₄ is its tendency to carry with it other substances, as alkaline and alkaline-earth nitrates, chlorates, sulphates, and chlorides. Potassium salts give more trouble in this respect than sodium salts. The precipitate may also contain silica, and basic, ferric, aluminic, or chromic compounds.

Repeated boiling up with very dilute HCl assists in removing some of these to a considerable extent, though there is some danger of dissolving some of the precipitate by this treatment. Washing alternately with hot dilute HCl and with cold water is often advantageous. Stolba's method of purifying the precipitate consists in digesting (after washing) for ten to fifteen minutes at a boiling heat, with 40 to 50 c. c. of cold saturated solution of Cu(C₂H₃O₂)₂.

and acetic acid, filtering, and washing free from Cu (*vid.* Crooke's *Select Methods*, 3d Ed., p. 484). Sloane recommends for purification from iron to decant the supernatant liquid closely, then add 5 to 10 c.c. of concent. HCl, and boil for one minute, dilute, and after nearly neutralizing with ammonia, filter and wash thoroughly (*Jour. Am. Chem. Soc.*, III., 37). Archbutt advises to precipitate warm (not boiling), allow to stand until thoroughly cold and the precipitate has settled well, then to filter and wash with cold water (*Jour. Soc. Chem. Ind.*, IX., 25). Jannasch and Richards assert that no correct determination of SO₃ can be made in the presence of Fe, because the precipitate always contains more or less of a double barium iron sulphate, from which SO₃ is expelled on ignition. To avoid errors they therefore recommend the previous removal of the iron by ammonia (*Jour. Pr. Chem.* [2], XXXIX., 321), (*vid.* also Lunge, *Zts. Angew. Chem.*, 1880, 473). Ziegeler (*Pharm. Centr.*, 1881, p. 555) recommends the addition of some AgNO₃ to the solution (containing chloride) that the AgCl may enclose, and carry with it the particles of BaSO₄. After washing with water the AgCl may be dissolved off with ammonia.

Mar recommends, for removal of alkaline salts, to dissolve the (washed) precipitate in conc. H₂SO₄, evaporating to dryness and washing.

SiO₂ in the precipitate may be removed by treating the ignited precipitate with HF and H₂SO₄, and re-igniting. An excess of H₂SO₄ is necessary.

Ign.—With C some BaS invariably forms. The difficulty may be remedied by adding a few drops of fuming HNO₃ to reoxidize the S, and igniting again, or better by reigniting after the addition of a drop or two of conc. H₂SO₄.

BaCO₃.

Rem.—At first amorphous, it assumes almost immediately the crystalline form, in which condition it does not affect alkalimetric indicators.

Cond.—Alkaline solution.

Sol.—Soluble in water containing CO_2 and in acids. Also taken into solution by NH_4Cl and some other ammonium salts, especially on boiling. Insoluble in a mixture of ammonium hydrate and carbonate.

Contam.— MgCO_3 , if much is present, and carbonates of fixed alkalies if present.

Ign.—Converted imperfectly to BaO , unless mixed with carbon, when the change occurs readily.

BaCrO₄.

Rem.—Reagent preferably $\text{K}_2\text{Cr}_2\text{O}_7$. Of service in separating Ba from other alkaline earths. Used chiefly in separation. Dissolving in HCl , adding KI , and titrating the I liberated is not usually satisfactory for quantitative estimation of Ba.

Cond.—Solution acid with acetic—no free mineral acid. Should contain only alkalies and alkaline earths.

Sol.—Dissolved by mineral acids, or very strong acetic.

Contam.— SrCrO_4 , if the ratio of Sr to Ba is greater than 1 to 5 or 6. In neutral solutions K_2CrO_4 affords a precipitate containing some of the precipitant. Metallic chromates may accompany the precipitate if members of the $(\text{NH}_4)_2\text{S}$ group or H_2S group are present.

Ign.—Decomposed to an indefinite extent. Unsuitable for determinations by ignition.

Fe₂(OH)₃.

Rem.—Precipitation in most cases effected by NH_4OH .

When but little ferrous iron is present, and heat is applied, a finely-divided red ("brick-dust") precipitate separates, which is insoluble except in concentrated HCl .

In presence of a larger proportion of ferrous salt, black $\text{Fe}_3(\text{OH})_2 = \text{Fe}(\text{OH})_2$, $\text{Fe}_2(\text{OH})_3$ will separate. With more ferrous salt the precipitate is green, the color being lighter the larger the proportion of ferrous salt; and when the iron is all absolutely in the ferrous form, the precipitate is

white. Whenever ferrous salt is present, a double ammonium ferrous salt forms, which remains in solution from which the iron slowly precipitates by absorption of oxygen, and conversion to the ferric form. NH_4Cl favors the precipitation of $\text{Fe}_2(\text{OH})_6$.

Cond.—Iron should be in ferric form. H_2S should be absent.

Sol.—Soluble in acids and in solution containing citric, tartaric acids, etc., as well as other organic substances, glycerine, sugar, etc. Insoluble in alkalies.

Contam.—Basic ferric salts, especially basic sulphate, unless the precipitant is in moderate excess. When precipitated by fixed alkalies, the precipitate contains some alkali, which is washed out with great difficulty. Precipitate will carry with it phosphoric acid as $\text{Fe}_2(\text{PO}_4)_3$, in nearly sufficient quantity to form that compound. The excess of phosphoric acid will remain in solution unless some other base (Al, Ca, etc.) is present to carry it down in combination. Precipitate may also contain nearly if not quite all of the Al, Mn, and silica present. Mg, Co, Ni, Zn, and Cu are also liable to be present in the precipitate, Ca also as CaCO_3 , if the alkaline solution has absorbed any CO_2 from the atmosphere. From these latter (Mg, etc., including Ca), the precipitate may be freed by one or more re-solutions and reprecipitations.

Ign.—Converted to Fe_2O_3 , with C, a partial reduction to Fe_3O_4 may occur. Fe_2O_3 is restored by adding a few drops of HNO_3 , and reignition. In contact with NH_4Cl , may form volatile Fe_2Cl_6 .

$\text{Fe}_2(\text{OH})_6(\text{C}_2\text{H}_3\text{O}_2)_6$. Basic Ferric Acetate.

Rem.—Ferrous salts, if present, are not precipitated. If in very small proportion, they may induce the formation of the "brick-dust" precipitate alluded to under $\text{Fe}_2(\text{OH})_6$. In analysis of iron ores and manufactured irons, the reduction of the major part of the iron to the ferrous form, and application of the basic acetate, separation is frequently

resorted to in order to remove the excess of iron, before determining phosphorus.

Cond.—The *dilute* solution should contain but little free acetic acid. The (ferric) iron should be in the form of acetate. This is obtained by neutralizing the free mineral acid present and adding $\text{NaC}_2\text{H}_3\text{O}_2$. No precipitate should appear in the cold, but on boiling a few minutes (three to five) it separates completely, provided not too much free acetic acid is present. *Too-long boiling* causes the precipitate to assume a form which filters with some difficulty.

Sol.—Soluble in cold dilute acetic acid and in mineral acids, also in citrates, and other organic substances mentioned as solvents of $\text{Fe}_2(\text{OH})_6$.—Insoluble in hot acetic acid only when quite dilute.

Contam.—Salts of fixed alkalies. Silica, alumina salts, and P_2O_5 , the latter in the form of $\text{Fe}_2(\text{PO}_4)_3$, [see $\text{Fe}_2(\text{OH})_6$]. The precipitate may also contain some Mn, Zn, Ni, Co, or Cu. Mn is more likely to be present if the amount of $\text{NaC}_2\text{H}_3\text{O}_2$ added was large. The amounts of these last in the precipitate is much diminished by increasing the proportion of free acetic acid in the solution. The danger of having sufficient free acid to prevent the precipitation of all the iron is, however, considerable. By redissolving in HCl, neutralizing, adding $\text{NaC}_2\text{H}_3\text{O}_2$ and reprecipitating, the Zn, Ni, etc., can be removed. Zn usually gives the most trouble. If much is present, it may be advisable to precipitate in a solution containing enough free (acetic) acid to hold a little Fe in solution. The latter may be separated by evaporating the excess of acid from the filtrate. SiO_2 and Cu should be previously removed by known methods, if their presence in the precipitate will influence subsequent work.

When chromium is present in the solution the action is peculiar. When iron predominates decidedly, all of the chromium is precipitated with it. If the ratio of chromium to iron is nearly the same, not only much of the chromium, but some of the iron is retained in the solution.

$Al_3(OH)_3$.

Rem.—In general terms the precipitate is very similar to $Fe_3(OH)_3$, but is more easily prevented from forming, and when separated, being more gelatinous in character, is less readily managed. Usual precipitant, ammonia.

Cond.—Neutral or slightly alkaline solution, containing preferably NH_4Cl . Addition of a little $(NH_4)_2S$ favors the separation.

Sol.—Dissolves in acids, and in fixed caustic alkalis; somewhat soluble in ammonia, especially in the cold. From this solution it may be separated by boiling out the major part of the NH_3 , particularly if NH_4Cl is present. Precipitation prevented by presence of tartrates, citrates, sugar, glycerine, etc. After boiling or standing for a short time, the precipitate will dissolve in acids (even HCl) slowly and with some difficulty.

Contam.—Basic Al salts, especially the sulphate. Retains P_2O_5 in proportion sufficient to form $Al_3(PO_4)_3$. May also contain Fe, Mn, or SiO_2 (hydrated). Possibly, also, Mg, Zn, Co, Ni, Cu, etc., from which last it may be freed by re-solution and reprecipitation. Ca may also accompany it as $CaCO_3$, if the alkaline solution has absorbed CO_2 .

Ign.—Converted to Al_2O_3 . Ignited with NH_4Cl some volatile Al_3Cl_3 may form. After ignition practically insoluble in HCl . Converted to a soluble form by fusion with an alkaline flux.

$Al_3(PO_4)_3$.

Rem.—Of service in the determination of Al in manufactured irons and in mineral phosphates. Under some conditions the precipitate appears to be $7Al_2O_3, 6P_2O_5$. (See p. 174.)

Cond.—Fe, if present, should be in the ferrous form. The conditions usually produced are a solution acid with acetic, in which Fe has been reduced by $Na_2S_2O_3$, and containing an excess of alkaline phosphate. This is boiled for some time.

Drown and McKenna (*Trans. A. I. M. Eng.*, XX., 242) find that this precipitate as produced by the conditions under which they worked has apparently the composition $7\text{Al}_2\text{O}_3$, $6\text{P}_2\text{O}_5$ (containing 24.14 per cent Al). Glaser (*Fres. Zts. Anal. Chem.*, XXXI., 383) states that $\text{Al}_3(\text{PO}_4)_3$ precipitates at 70°C . or below, and at the boiling heat the precipitate consists of a mixture of neutral and basic salt.

Sol.—Dissolves in mineral acids. Insoluble in moderately strong HCl , H_2O_2 . Prevented by tartrates, citrates, etc., in the same way as $\text{Al}_3(\text{OH})_3$.

Contam.— $\text{Fe}_3(\text{PO}_4)_3$ and possibly basic ferric salt. If Fe is kept entirely in the ferrous condition (which is not always possible) this contamination would not occur. Remedied by redissolving, reducing, and reprecipitating. $\text{Ca}_3(\text{PO}_4)_2$ (or alkaline salts if the solution is not sufficiently dilute) may also accompany the precipitate. Remedy by re-solution and reprecipitation. Glaser's method for mineral phosphates involves the previous separation of the lime, as CaSO_4 , by the aid of alcohol (*Zts. Angew. Chem.*, 1889, p. 636).

$\text{Al}_2(\text{OH})(\text{C}_2\text{H}_3\text{O}_2)_3$. *Basic Alumina Acetate.*

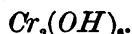
Rem.—Very similar to the corresponding Fe compound. Being more slimy in character, it gives more trouble in filtering and general management. Used for separation only.

Cond.—The same as for the Fe compound. Practically no free acetic acid is admissible. Al should be in the form of acetate. Precipitate obtained by boiling. If boiled too long, it filters and washes with more difficulty.

Sol.—Dissolves in acids, to some extent in very dilute boiling acetic. If the solution after boiling is allowed to cool, a considerable proportion redissolves. Soluble or precipitation prevented by citrates, tartrates, etc. The small amount almost invariably remaining in the filtrate may be recovered by careful neutralization and boiling,

or better by evaporating to dryness, and taking up with dilute acetic.

Contam.—As for the Fe compound. Salts of fixed alkalies, P_2O_5 , [in proportion sufficient to form $Al_2(PO_4)_3$], SiO_2 (hydrated), Mn, Zn, etc.



Rem.—In general properties this precipitate resembles $Al_2(OH)_2$ and its management is similar. Its tendency to carry with it other substances requires that it shall always be redissolved and reprecipitated with ammonia at least twice.

Cond.—Absence of members of $(NH_4)_2S$ groups and preferably of all non-volatile salts. Solution must be exactly neutral (ammonia added in slight excess and then boiled until neutral). Addition of a little $(NH_4)_2S$ is of advantage. NH_4Cl assists the separation.

Oxidizing agents, as H_2O_2 , Cl, etc., should be absent, since in alkaline solutions they afford chromates.

Sol.—Dissolves in all acids, in fixed alkaline hydrates, and perceptibly in excess of NH_4OH . Soluble or prevented from precipitating by tartrates, citrates, sugar, etc.

Contam.—Salts of fixed alkalies, alkaline earths, members of the $(NH_4)_2S$ group, etc. (See above, *Rem.*)

Ign.—Converted to Cr_2O_3 , in which form, if strongly ignited, it becomes insoluble in HCl. In presence of fixed alkalies or alkaline salts, and at the same time in contact with the oxygen of the air, is partially or entirely converted to chromate.



Rem.—Two forms, one tolerably easily soluble in acids, the other insoluble, except in very strong acids or by fusion, are known to exist. The “insoluble” form is obtained by boiling the solution acid with sulphuric.

Cond.—Dilute solution containing but little free H_2SO_4 . HCl and chlorides should be absent. Long boiling is necessary, the bulk of the solution being maintained.

Fe, if present, should be in the ferrous form. $\text{HC}_2\text{H}_3\text{O}_2$ favors the precipitation.

Sol.—The soluble form is attacked by the same solvents as $\text{Fe}_2(\text{OH})_6$. The “insoluble” form is slowly soluble in hot concentrated HCl or H_2SO_4 , or by fusion with KHSO_4 .

Contam.— Fe_2O_3 , Al_2O_3 , SiO_2 , and P_2O_5 . Some iron inevitably is converted to Fe_2O_3 , and separates with the precipitate. By re-solution, reducing, and reprecipitation almost all can be removed. Al_2O_3 is prevented from contaminating the precipitate by the larger proportion of free acid. SiO_2 may be expelled after ignition by treating with HFl (or NH_4Fl) and H_2SO_4 . P_2O_5 by fusion, for some little time, with Na_2CO_3 , and washing with dilute Na_2CO_3 solution, which leaves behind Na_2TiO_4 , soluble in acids.

Ign.—Converted to TiO_2 . Retains some SO_2 ; removable by adding a few pieces of solid ammonium carbonate and re-igniting. Volatilized by ignition with HFl , alone, or with an insufficient amount of H_2SO_4 .

$(x\text{Na}_2\text{O}, \text{TiO}_2)$ or Na_2TiO_4 . *Sodium Titanate.*

Rem.—Usually obtained by fusing material containing TiO_2 and P_2O_5 for some time, to convert them into sodium salts, and then to separate them by lixiviation. Chiefly of service as a step in the determination of phosphorus in titaniferous ores.

Cond.—Long fusion at a fairly high temperature is necessary. A repetition of the fusion of the portion insoluble in water, with a fresh lot of sodium carbonate, is at least necessary in order to prove the efficiency of the first fusion.

Sol.—Dissolved by acids; to some extent by water alone. Insoluble in solution of Na_2CO_3 . The washing (leaching) of the insoluble portion should be continued until the washings begin to run cloudy.

Contam.—As usually applied to iron ores or precipitates from solutions thereof, the insoluble residue may contain,

besides sodium titanate, Fe_2O_3 , acid sodium silicates, alkaline-earth carbonates, etc.

$2\text{ZnCO}_3 \cdot 3\text{Zn}(\text{OH})_2$. *Basic Zinc Carbonate.*

Rem.—Usual precipitant, Na_2CO_3 . Flocculent at first, becoming more granular by boiling.

Cond.—Solution should not contain caustic or bicarbonated alkalies or any ammonia salts. If CO_2 is evolved by addition of the reagent, it must be boiled out. Only fixed alkalies besides the zinc should be present.

Sol.—Dissolved by dilute acids, fixed caustic alkalies, bicarbonates, and ammonia salts; also by organic solutions. A very large excess of fixed alkaline chlorides hinders or partially prevents the precipitation. Insoluble in water and small amounts of fixed alkaline carbonates.

Contam. — Alkaline carbonate, necessitating several washings by decantation with boiling water to remove it. Fe_2O_3 , — Al_2O_3 , — SiO_2 . By dissolving the precipitate in HCl after ignition Al_2O_3 and SiO_2 are left insoluble; on precipitating the solution with ammonia, redissolving, and reprecipitating two or three times, $\text{Fe}_2(\text{OH})_6$ is separated. These impurities may then be ignited, weighed, and deducted.

Ign.—Converted to ZnO , which in itself is not volatile. In contact with C or reducing substances metallic zinc which is volatile may be formed.

ZnNH_4PO_4 .

Rem.—Usual precipitant, $\text{NaNH}_4\text{NPO}_4$. Some prefer Na_2HPO_4 in presence of ammonium salts. The best method of procedure is to add the alkaline phosphate to the acid solution, and then to neutralize the hot solution by adding ammonia, little by little, finally to heat, immersing the beaker in a boiling-water bath, until free NH_3 is expelled and the precipitate is crystalline. The solution containing the precipitate cannot be boiled without bumping vigorously. The precipitate can be dried at 100°

and weighed as ZnNH_4PO_4 , or ignited and weighed as $\text{Zn}_3\text{P}_2\text{O}_8$.

Cond.—Oxalates should be absent. Large excess of ammonium chloride or acetate should be particularly avoided. Practically, the solution should only contain alkalies besides the zinc.

Sol.—Dissolved by acids, excess of ammonia, ammonium oxalate, chloride or acetate, especially if hot. The solvent effect of the chloride and some other ammonium salts is to a very great extent diminished by the use of an excess of alkaline phosphate (about three times as much as is required to afford the compound).

Ign.—If heated up too rapidly, some loss may be experienced. In contact with C a partial reduction to metal and consequent loss may occur. The precipitate should be carefully separated from the filter-paper and the same burned separately, or it may be dissolved by means of dilute nitric acid into a weighed capsule and the solution evaporated and finally ignited.

After ignition the precipitate is usually opaque, white, somewhat sintered together; sometimes, without apparent reason, it fuses to a glass.

ZnS.H₂O.

Rem.—Usual precipitant, H_2S in neutral solution, or one acid with some organic acid (acetic, citric, formic, etc.). Precipitation can be effected (though slowly) in H_2SO_4 solution; the smaller the proportion of free H_2SO_4 , the more complete the separation. NH_4Cl favors its separation in a granular form, and checks a tendency to run through the filter-paper, which it sometimes exhibits, especially when the solution contains free ammonia. Oxidizes slowly on exposure to the air.

Cond.—Solution should be alkaline or acid only with some of the weaker organic acids. Free mineral acids prevent the precipitation to a greater or less extent. H_2SO_4 has the least effect, HCl the greatest. Boiling

facilitates the formation of the precipitate, but increases the solvent power of acids upon it. Fe should be absent.

Sol.—Dissolved by dilute HCl and HNO₃, or by moderately strong H₂SO₄ when hot. Insoluble in alkalies, neutral solutions, and in organic acids, though the latter, when in excess, retard somewhat its formation. Free ammonia has a similar effect.

Contam.—MnS or Ni, Co and Fe sulphides. Fe should be separated previously. From the others it may be freed by re-solution, neutralizing, and reprecipitating.

MnCO₃·H₂O.

Rem.—Na₂CO₃, usual precipitant. When precipitated cold, white, and flocculent; by boiling becomes granular and assumes a light brownish shade, probably from oxidation.

Cond.—Solution should not contain bicarbonates or ammonia salts. If CO₂ is evolved by the addition of the precipitant to an acid solution, it must be boiled out. Solution must be rendered alkaline by the reagent.

Sol.—Dissolved by dilute acids, bicarbonates, ammonia salts, and solutions containing citrates, tartrates, sugar, etc. Also by solutions containing large amounts of fixed alkaline salts.

Contam.—Alkaline carbonate, requiring several washings (by decantation) with boiling water to remove it.

Fe₂O₃; removed by repeated solution in HCl and reprecipitation with ammonia after igniting the precipitate. SiO₂, by dissolving the ignited precipitate in acid and filtering off.

Ign.—In contact with air gives black Mn₂O₃, non-volatile. Recent investigations tend to show that the composition is not absolutely constant. If alkali has not been washed out, ignition in contact with the air affords alkaline manganate.

MnNH₄PO₄.

Rem.—Usual precipitant, NaNH₄HPO₄, or Na₂HPO₄, in presence of ammonium salts. Best managed by adding

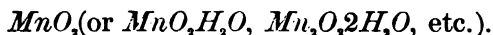
the reagent to the *acid* solution of Mn, boiling, and then adding ammonia little by little to the boiling solution until a slight excess is present, then heating on the water-bath until the precipitate assumes *completely* the crystalline form.

Cond.—The Mn must be entirely in manganous form, and solution alkaline, though not strongly so. An excess of phosphate (about three times as much as is required to form the combination) must be present. Oxalates should be absent, as well as excessive amounts of ammonia salts or free ammonia.

Sol.—Dissolved by acids. Somewhat soluble in decided excess of ammonia, in NH_4Cl and some other ammonium salts. The solubility in these last is neutralized by the presence of an excess of the precipitant. When too large proportion of ammonia is present, the precipitate, which should be white or faintly pinkish, becomes deeper in color, sometimes quite brown.

Contam.—Practically none if bases forming insoluble phosphates are absent and moderate care is used in washing.

Ign.—Converted to $\text{Mn}_2\text{P}_2\text{O}_7$. The temperature should not be too rapidly raised or there may be some loss. The peculiar nacreous lustre of the precipitate is more pronounced after ignition. Sinters somewhat. Not volatile.



Rem.—For separation in two separate cases. 1. From acetate solution by addition of an oxidizing agent, usually Br. 2. From a boiling solution in nitric acid by addition of crystals of KClO_4 . Also (3) obtained in titration by the Volhard method—adding standard (volumetric) solution of $\text{K}_2\text{Mn}_2\text{O}_8$ to a solution neutralized by ZnO . In all cases the precipitate probably contains some water of constitution (hydrated oxide).

Cond.—Absence of HCl or other halogen acids, lower oxides of nitrogen or reducing agents. In Case 1 a fair

proportion of alkaline acetate must be present, to supply base to the mineral acid which might otherwise be set free. Boiling solution necessary.

Sol.—Dissolved or prevented from forming by dilute mineral acids, particularly HCl. Insoluble in moderately strong acetic or in concentrated nitric. When formed, it is soluble in strong HCl, forming temporarily an olive-green solution of Mn_2Cl_2 , which becomes practically colorless $MnCl_2$ by heating. Readily dissolved by HCl or H_2SO_4 in presence of reducing agents (SO_2 , $H_2C_2O_4$, $FeSO_4$, etc.).

Contam.—Salts of fixed alkalies, Fe_2O_3 , ZnO .

Ni (Electrolytic).

Rem.—Requires a stronger current than Cu—two or three Bunsen cells (12 to 14 c. c. oxyhydrogen gas per minute). The rapid deposition of the metal is somewhat checked as soon as a coating of nickel has formed, tending to be slower the thicker the coating. This peculiarity is most marked in cold solutions. In preparing for weighing it is treated as electrolyzed Cu, by washing with water, then with alcohol, and drying at a gentle heat.

Cond.—Solution should contain no other metals of the $(NH_4)_2S$ or H_2S groups. Chlorides should be preferably absent. The solution should contain the nickel as double ammonium nitrate, sulphate, or oxalate (the latter most advantageous), and excess of ammonia. The operation is more rapid at $70^\circ C$. In consequence ammonia requires to be added from time to time.

Sol.—Dissolves readily in HNO_3 , especially with the aid of heat. Slowly soluble in strong solution of $(NH_4)_2C_2O_4$.

Contam.—Co, Fe, and Zn, being precipitated from oxalate solution under the same or similar conditions, may be present in the coat unless previously separated.

Ni(OH)₂ and Ni₂(OH)₄.

Rem.—Usual precipitant, KOH or NaOH. If the solution contains free halogens, or hypochlorites, hypobro-

mites, etc., $\text{Ni}(\text{OH})_2$ may be precipitated *black*. The most marked characteristic of the precipitate is the persistency with which it takes up and retains impurities derived from the solution.

Cond.—No bases other than fixed alkalies should be present.

Sol.—Dissolved readily by mineral acids. Soluble or prevented from precipitation by NH_4 salts and tartrates, citrates, etc., or other organic solutions.

Contam.—Alkali used as the precipitant, Fe_2O_3 , Al_2O_3 , and silica from the reagents. The precipitate requires thorough washing by decantation with boiling water. After ignition and weighing it should be dissolved in HCl , which leaves SiO_2 and Al_2O_3 . From this solution the iron should be precipitated by ammonia, filtered, redissolved and reprecipitated again, and these impurities ignited, weighed, and the weight deducted.

Ign.—If only moderately, some Ni_2O_3 is contained in the precipitate. If strongly ignited, it all becomes *green* NiO . The tint is not a pure green like that of ignited Cr_2O_3 , but lighter, and somewhat muddy.

NiS. H₂O.

Rem.—For separation only. Usual precipitant, H_2S in weak acetic solution, or $(\text{NH}_4)_2\text{S}$ followed by acetic acid in excess. Oxidizes easily in contact with the air, with partial formation of NiSO_4 . Should be washed by and kept in contact with H_2S water during manipulation.

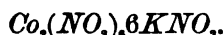
Cond.—Absence of other members of $(\text{NH}_4)_2\text{S}$ or H_2S group. NH_4Cl in the solution assists materially its separation in the granular form. Free ammonia, on the other hand, tends to keep the precipitate suspended in the liquid. The solution should be only slightly acid with acetic acid, or else barely alkaline.

Sol.—Formation of the precipitate prevented by moderate amounts of free acetic acid or mineral acids. When once formed, it is insoluble in these menstrua unless oxi-

dized by exposure to air, which may easily occur. Somewhat soluble in $(\text{NH}_4)_2\text{S}$. To meet these peculiarities of the compound, the solution should be rendered alkaline with ammonia, and H_2S passed in, or $(\text{NH}_4)_2\text{S}$ added, and when the precipitate is *fully formed* the solution is acidified with acetic acid, and the precipitate allowed to settle (which occurs readily if NH_4Cl is present) warming facilitates the separation. Soluble in hot HNO_3 , or in aqua regia. Soluble in KC_2O_4 .

Contam.—Sulphides of $(\text{NH}_4)_2\text{S}$ group, if not previously separated.

Ign.—Gives mixture of oxide and sulphate.



Rem.—Usual precipitant, KNO_3 , in a solution slightly acid with acetic. Yellow crystalline precipitate, forming best in a warm solution.

Cond.—Solution should contain only Co, Ni, and K salts. It should be a nearly saturated solution of $\text{KC}_2\text{H}_3\text{O}_6$, containing but little free acetic acid.

Sol.—Dissolved by H_2O , acids, NH_4 salts, NaCl , and most other Na salts. Insoluble in $\text{KC}_2\text{H}_3\text{O}_6$, and other K salts. Insoluble in dilute acetic, and in alcohol. The precipitate should be first washed with a 10 per cent solution of $\text{KC}_2\text{H}_3\text{O}_6$, and the latter salt finally removed by washing with alcohol.

Contam.—If Ca or other alkaline earths are present, a yellow NiCa nitrite, similar in properties (solubility, etc.) to the Co compound, will separate. Pb also gives a similar compound. Care in washing off K salts is necessary.

Ign.—By addition of H_2SO_4 and ignition the precipitate is converted to $3\text{K}_2\text{SO}_4 + 2\text{CoSO}_4$. One method of management consists in dissolving the washed precipitate through the filter with a little hot dilute H_2SO_4 into a weighed capsule, evaporating and igniting. Some KHSO_4 ,

may remain after ignition; removed by addition of a small lump of solid ammonium carbonate and igniting.

CoSH₂O.

Rem.—For separation only. Properties essentially the same as those of NiS.H₂O. Precipitant, H₂S in weak acetic solution, or (NH₄)₂S. Oxidizes readily in the air when moist, some sulphate being formed. Should be kept in contact with H₂S water during filtration.

Cond.—Absence of other members of (NH₄)₂S or H₂S group. NH₄Cl assists the separation. Unlike NiS.H₂O, free NH₄OH does not materially influence the separation. Solution should be preferably *slightly* acid with acetic before filtration (*vid.* NiS.H₂O).

Sol.—Formation of the precipitate prevented by moderate amounts of free acetic or mineral acids. When once formed, however, it is insoluble in these menstrua. Of the ordinary mineral acids, HCl has the strongest preventive effect, H₂SO₄ the least; but a very small amount of free H₂SO₄ retards the separation markedly. Soluble in hot HNO₃, or in aqua regia; also in KCy.

Contam.—Usually accompanied by Ni or other members of the group if not previously separated.

Ign.—Affords mixture of oxide (Co₂O₃) and sulphate.

Cu.

Rem.—Obtained by electrolytic deposition on platinum from acid solution. Free HNO₃ gives a bright coating. Too strong a current gives a spongy, imperfectly adherent coat.

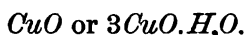
Cond.—Sulphuric acid solution preferable, with or without a few drops of nitric acid. Not over 8 per cent of free acid should be present. Chlorides disadvantageous. Organic acids (as citric, etc.) should not be present, since they afford a brittle deposit containing organic elements.

Sol.—Easily soluble in HNO₃. When that acid is present, at the end of the operation, flood out the dish with

water before breaking the current. Deposit dissolved or prevented from forming by Cl, lower oxides of nitrogen, or too strong acid.

Contam.—If free HNO_3 is absent, As, Sb, or Bi may occur in the deposit, rendering it blackish. A black coloration is, however, sometimes due to other causes. If free HNO_3 is present, Zn, if present, begins to deposit (imperfectly) as soon as all the Cu is precipitated. Pb and Mn may separate from the solution on the other pole, as PbO_2 or MnO_2 , and in case a dish is used these oxides may fall to the bottom and be caught in the deposit. $\text{SnO}_2 \cdot (x\text{H}_2\text{O})$ may also separate from the solution and be caught in the deposit in the same way.

Ign.—Easily oxidized by heating in air or oxygen. After deposition and washing with water the water should be rinsed off with alcohol, the alcohol drained off, and the dish dried at a temperature which can be borne by the hand, not higher.



Rem.—Usual precipitant, KOH or NaOH in a boiling solution or one subsequently boiled. Na_2CO_3 or K_2CO_3 may also be used in the same manner. The precipitate, at first the light bluish hydrate or basic carbonate, becomes black on boiling from elimination of H_2O .

Cond.—Alkaline solution, not containing bases, the hydrates of which are more or less insoluble. NH_4 salts and organic substances should be absent.

Sol.—Dissolved by acids; also by NH_4 salts and organic solutions, as citrates, etc. Precipitation prevented by alkaline bicarbonates, especially by KHCO_3 .

Contam.—Chiefly the alkali of the precipitant, which is washed out with great difficulty. Some SiO_2 dissolved by the reagent from the bottle in which the reagent was kept, or otherwise introduced, may also be present. Left behind on dissolving in acid the ignited and weighed precipitate.

Ign.—Obtained as black CuO. Some reduction to the

metallic form by contact of C may occur, but as the metal is not volatile it is readily restored by ignition with a few drops of HNO_3 . The use of platinum crucibles where reducing substances may be mingled with the precipitate is inexpedient. Precipitate quite hygroscopic after ignition.

CuS.

Rem.—Usually for separation. When for determination, treated as suggested under "*Ign.*" for production of Cu_2S . Has ordinarily a brown to blue-black color, but when precipitated along with sulphur, has an orange-red color.

Cond.—Acid solution usually used, though not indispensable. Precipitation can be effected promptly in presence of moderately strong H_2SO_4 , or of HCl if not too strong or hot. If HNO_3 is present, the solution must be dilute and cold.

Sol.—Soluble in hot dilute HNO_3 , and in HCl when hot and moderately strong. Somewhat soluble in $(\text{NH}_4)_2\text{S}$, especially if polysulphides are present. Insoluble in HCl or H_2SO_4 , or in NaHS or KHS , unless polysulphides are present. Soluble in KCy .

Ign.—Partly reduced to Cu with C . Converted to Cu_2S by mixing with sulphur and igniting in a current of hydrogen (in a Rose crucible).

PbSO₄.

Rem.—Usual precipitant, H_2SO_4 . By digestion with alkaline carbonates or bicarbonates it is converted to PbCO_3 .

Cond.—Solution should be acid with H_2SO_4 and contain little or no free HNO_3 or HCl . The larger the proportion of these acids and the warmer the solution the more H_2SO_4 required. NH_4 salts and salts of organic acids should not be present. Also, any large proportion of chlorides.

Sol.—Readily soluble in concentrated mineral acids,

H_2SO_4 , as well as the others, but less soluble in dilute H_2SO_4 than in pure water. Soluble in $\text{Na}_2\text{S}_2\text{O}_3$, in caustic alkaline solutions, and in ammonia salts, notably those of organic acids, especially when free ammonia is present. $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ and $(\text{NH}_4)_2\text{C}_2\text{H}_3\text{O}_2$ may be used for this purpose. To obtain PbSO_4 for ignition and weighing, the usual procedure is to wash off all other substances with very dilute H_2SO_4 and then to remove the latter before drying by washing with alcohol.

Contam.—If all other sulphates (than PbSO_4) have not been removed by washing with dilute H_2SO_4 , as just described, the precipitate may be contaminated with sulphates, most of which are insoluble in alcohol.

Ign.—Unchanged by a moderate heat. At temperatures usually higher than are ordinarily obtained with a Bunsen burner, the compound may fuse, but without volatilization.

With C partially or entirely reduced to Pb, PbS , etc., which are volatile. The precipitate should be separated from the filter-paper, which should be separately incinerated (in the cover of the *porcelain* crucible) with the aid of a few drops of concentrated HNO_3 and H_2SO_4 , the ashes and precipitate united, and the whole ignited before weighing.

PbCrO₄.

Rem.—Usual precipitant, $\text{K}_2\text{Cr}_2\text{O}_7$ in solution acid with acetic.

Cond.—Bi, Ba, Ag, and Fe should not be present. Solution should not contain chlorides or large amounts of alkaline salts, and should be acid with no stronger acid than acetic. Alkaline citrates, tartrates, etc., should be absent.

Sol.—Dissolved by moderately strong mineral acids and by caustic alkalis. HCl reduces the chromium partially or entirely to Cr_2Cl_6 , more readily in the presence of acetic acid, alcohol, or other carbon compounds. Soluble in hot

moderately concentrated solutions of $(\text{NH}_4)\text{C}_2\text{H}_3\text{O}_2$. Insoluble in very dilute HNO_3 .

Ign.—Alone fuses and parts with some oxygen. With C it is more easily decomposed, some metal being reduced. On account of these properties the precipitate is usually dried on a weighed filter for estimation. The Gooch filter, in which, if paper is used, it need be only about the size of a five-cent coin, is especially advantageous for this purpose.

PbS.

Rem.—Usual precipitant, H_2S . Partially decomposed by drying at 100°C . Used for separation.

Cond.—Solution may be slightly acid, neutral, or alkaline. HCl interferes most with complete separation, HNO_3 less, and H_2SO_4 least. If the solution is acid with any large proportion of these, the precipitation is best effected in the cold.

Sol.—Dissolved by dilute boiling HNO_3 , though that solvent almost invariably affords some PbSO_4 . Of concentrated acids hot HCl is the best solvent, since with either HNO_3 or H_2SO_4 some PbSO_4 will form in such a way as to protect a portion of the sulphide. Soluble in $\text{Na}_2\text{S}_2\text{O}_3$.

Ign.—Volatilized. Easily reduced to metal by ignition with C.

AgCl.

Rem.—For determination of Ag, usual precipitant, HCl . For determination of Cl, usual precipitant, AgNO_3 . Separates most readily in presence of an excess of silver salts. Partially decomposed by heating with strong HNO_3 or H_2SO_4 . Darkens in strong daylight, more quickly in sunlight, but may become very dark without material loss of weight.

Cond.—Acid solution; absence of any notable quantities of alkaline chlorides or other alkaline salts.

Sol.—Partially dissolved by moderately strong and hot HCl or HNO₃. Somewhat soluble in alkaline and alkaline-earth chlorides and nitrates. Readily soluble in NH₄OH, in KCy, and in Na₂S₂O₃. In the latter less readily if the substance has been changed by light.

Ign.—Fuses at a low temperature (dull red) and volatilizes at a little higher temperature. Easily reduced to metal by strong heat, especially when mixed with Na₂CO₃ or C. On burning the filter-paper (which should be separated from the precipitate) the ash should be treated with HNO₃ to obtain AgNO₃, then a drop or two of HCl, is added to restore AgCl and the whole after drying cautiously, heated to incipient fusion.

As₂S₃ and As₂S₅.

Rem.—Usually precipitated by H₂S in HCl acid solution. From the solution of arsenic sulphides in alkaline polysulphide the addition of acid separates As₂S₃. As₂S₅ requires very thorough drying before weighing, the last portions of water being driven out with difficulty.

Cond.—Solution acid, with some mineral acid (HCl preferable). As should be in triad form. If in pentad form, it is slow to reduce and precipitate (As₂S₅ + S₂) by prolonged action of H₂S and warming.

Pentad arsenic is most readily and completely separated by placing the solution in a bottle, saturating with H₂S cold, then corking tight, and immersing the bottle in boiling water for about an hour. The precipitate under these conditions is As₂S₃, having essentially similar properties to As₂S₃.

Sol.—Dissolved by alkaline solutions (hydrates, carbonates, or sulphides); also by aqua regia, fuming nitric acid, water solutions of chlorine, bromine, etc. In a neutral solution scarcely any precipitation occurs. Insoluble in strong HCl, even on boiling. Practically insoluble in H₂SO₄. Dissolved by KHSO₄.

Ign.—Readily volatilized without change of composition.

MgNH₄AsO₄.

Rem.—Usual precipitant, MgCl₂ in ammonia solution containing alcohol. Precipitate white, crystalline, closely resembling MgNH₄PO₄.

Cond.—Solution alkaline with ammonia, containing a minimum amount of NH₄Cl, and 25 to 30 per cent of alcohol. No sulphates or other compounds partially or entirely insoluble in alcohol of this strength should be present. The As must be in pentad form (a condition realized in solutions containing alkaline polysulphides).

Sol.—Dissolved by acids or on application of heat. Somewhat soluble in water and in NH₄Cl, an effect partly neutralized by presence of ammonia and alcohol, in which it is insoluble.

Contam.—Basic Mg salts, sulphates, and other salts partially or entirely insoluble in diluted alcohol.

Ign.—Partially volatilized if heated up quickly. By slow heating it is dried and finally altered to Mg₃As₂O₇, which is non-volatile. With C partly volatile. A convenient method of management consists in dissolving the washed precipitate through the filter by dilute HNO₃ into a weighed capsule, evaporating, igniting slowly and finally intensely.

Sb₂S₃.

Rem.—Usually precipitated by H₂S in acid solution, or by acidifying solutions of sulphantimonite.

On drying the precipitate does not surrender all H₂O until the temperature is raised to 200° C., when it becomes black. This degree of heat is liable to char the paper when dried on a weighed filter.

By the action of oxidizing agents (Br, HNO₃, HgO, etc.) it is converted to Sb₂O₃.

Cond.—Solution slightly acid and moderately dilute. An excess of H₂S causes a more rapid separation of the precipitate. If too acid or too concentrated, the precipitation may be imperfect.

Sol.—Precipitate dissolved or prevented from forming

by moderately concentrated acids, especially HCl. H_2SO_4 has much less effect. The preventive effect is increased with the temperature. Tartaric acid in the solution assists precipitation.

Dissolved by fixed alkalies or alkaline sulphides.

Scarcely soluble in ammonium carbonate or KHSO_4 .

Somewhat soluble in $\text{H}_2\text{C}_2\text{O}_4$, but insoluble in it if boiled in presence of an excess of H_2S (separation from Sn).

Contam.—S usually accompanies the precipitate. To remove this the water is first displaced by alcohol, and the S dissolved out by CS_2 .

Ign.—Partially or entirely volatilized by ignition alone, or with reducing agents. Mixed with 30 to 50 times its weight of HgO and ignited, it is converted to Sb_2O_3 , which is stable at the ordinary temperature of ignition. Frequently, however, it is converted to Sb_2O_3 by Br or HNO_3 before ignition.



Rem.—Usually used in separating Sb quantitatively from Sn and As by fusing the oxides with NaOH (or Na_2CO_3) and nitrate. Also as a qualitative test for Na. In the latter case the reagent is KSbO_3 or $\text{K}_2\text{H}_2\text{Sb}_2\text{O}_7$, which should be freshly dissolved, as it alters by keeping in solution. Under ordinary conditions the crystalline precipitate forms rather slowly—favored by stirring.

Use of this compound as a quantitative test for Na has been proposed.

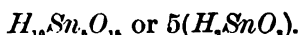
Cond.—Alkaline solution. Salts of the fixed alkalies only should be present. Large excess of K salts, especially K_2CO_3 , should be avoided. The addition of 30 per cent or more of alcohol assists the separation.

Sol.—Soluble in about 300 parts of water. Dissolved by alkaline salts, especially strong K_2CO_3 . Less soluble in alcohol. Dissolved by acids.

Contam.—Alkaline salts; also antimonates of alkaline earths and of the metals (Cu, etc.). The presence of

alkalies is unimportant when, as is usual, the *separation* of Sb is intended.

Ign.—Destroyed or decomposed.



Rem.—The above is called the “insoluble” form of hydrated stannic oxide, because not readily soluble. It is usually obtained by boiling slightly acid (HNO_3 or H_2SO_4) solutions containing the soluble form in partial suspension, or by boiling weakly acid solutions (of stannic compounds) containing neutral alkaline salts (NH_4NO_3 , $NaNO_3$, Na_2SO_4 , etc.). The presence of acetates assists the separation.

Cond.—HCl or chlorides should be small in amount, preferably entirely absent. Solution should be acid, tolerably dilute, and boiled for some time.

Sol.—The “soluble” form (obtained by neutralizing stannic solutions with caustic or carbonated fixed alkalies) is readily soluble in excess of the alkali or in acids. The “insoluble” form is only soluble with difficulty in HCl or in caustic alkali, and practically insoluble in dilute HNO_3 or H_2SO_4 .

Contam.—As and Sb oxides, which should have been removed previously. In analyses of bronzes, etc., CuO, removed by long digestion with dilute HNO_3 . SiO_2 , removable by treatment with HF and H_2SO_4 . Fe_2O_3 , removed by fusion with NaOH or Na_2CO_3 , and after further treatment by well-known methods, separating the Fe_2O_3 , which is weighed and deducted. This operation is usually performed upon a *weighed portion* of the precipitate.

P_2O_5 may also accompany the precipitate, being removable or determinable by a method similar to that for Fe_2O_3 . Digestion of the precipitate with $(NH_4)_2S$ or K_2S may also be applied to dissolve out metastannic acid, and leave behind CuS, FeS, etc., the Sn being separable from the solution as SnS_2 by acidification.

Ign.—Requires intense heating to remove all H_2O . Not

easily reduced to (volatile) Sn by C, though such reduction is possible on igniting the precipitate. Volatilized as chloride by ignition with NH_4Cl . Otherwise not volatile at high temperatures.

SnS₂.

Rem.—Usually precipitated by H_2S in acid solution, or by acidifying solutions of alkaline sulpho-stannate. Obtained for purposes of separation, or for determination as SnO_2 after oxidizing. Disposition to run through the filter checked by alkaline acetates or nitrates, etc.

Cond.—Solution slightly acid, moderately dilute. Precipitation promoted by acetates, interfered with by alkaline oxalates or oxalic acid.

Sol.—Moderately concentrated acids, especially HCl , dissolve or prevent precipitation. The influence is more marked the more concentrated the acid or the higher the temperature. Soluble in a boiling solution containing free $\text{H}_2\text{C}_2\text{O}_4$ (separation from Sb).

Ign.—If rapidly and strongly heated, some SnS_2 may be volatilized. By moderate heating with access of air SnO_2 forms without loss. It is, however, usual to assist the oxidation with a few drops of HNO_3 added from time to time.

The ignited precipitate may contain some H_2SO_4 after ignition, which is best removed by adding a little $(\text{NH}_4)_2\text{CO}_3$ and igniting again.

Ammonium Phospho-molybdate. $12\text{MoO}_3(\text{NH}_4)_3\text{PO}_4 +$.

Rem.—Yellow, finely crystalline precipitate. Precipitant, $(\text{NH}_4)_3\text{MoO}_4$ in HNO_3 solution. The ratio of MoO_3 to P_2O_5 in the precipitate varies according to the proportion of substances present in the solution (NH_4NO_3 , $\text{Fe}(\text{NO}_3)_3$, etc.), the proportion of free acid, the kind of acid, the length of time elapsing before filtering, and the temperature at which it is effected. With the same or closely similar conditions the ratio of MoO_3 to P_2O_5 is essentially the same. Precipitation promoted by agita-

tion. When precipitation is complete, the precipitate settles rapidly after stirring. Precipitated under the conditions described by Emmerton (volumetric determination of P in irons), the ratio of MoO_3 to P_2O_5 is 24 to 1.

Cond.—Solution should be acid with HNO_3 . Too much free HNO_3 retards or may prevent complete precipitation; too little allows Fe_2O_3 to come down with it, in which case the color is more orange. An excess of the precipitant should be present; also at least 10 gms. of NH_4NO_3 for every 0.1 gm. or less of P present. Temperature should be 70° to 85° C. Below 70° the separation is very slow, whereas on boiling (other conditions being right) MoO_3 or Fe_2O_3 may accompany the precipitate. Reducing agents, organic acids, silica, chlorides, and HCl should be absent. H_2SO_4 and sulphate retard precipitation. If the precipitate is to be dissolved for volumetric estimation in a solution of material containing but little iron, some iron should be added to give correct results, or the standard should be obtained in material of the same character. TiO_2 when present retards precipitation.

Sol.—Readily dissolved by NH_4OH and other alkalis; also by alkaline phosphates. If the ammonia is too strong, however, the solution will be turbid with $(\text{NH}_4)_2\text{MoO}_4$. Dissolved or decomposed by water alone, the more readily the higher the temperature. Precipitation prevented by tartaric acid or organic substances of that class. Somewhat soluble in HCl , or moderately strong H_2SO_4 and HNO_3 . Insoluble in weakly acid solutions and acid solutions of NH_4 salts. Solution for washing should contain 1 per cent HNO_3 and 10 per cent NH_4NO_3 , or a corresponding amount of H_2SO_4 and $(\text{NH}_4)_2\text{SO}_4$.

Contam.—Arsenio-molybdate, silica, Fe_2O_3 , TiO_2 , MoO_3 .

Arsenio-molybdate precipitates the less readily the lower the temperature. By allowing the solution to stand for about two days at 40° C. the phospho-molybdate may be precipitated free from arsenic. When present, however, As is separated either before or after.

Silica, either as hydrated SiO_2 , or as silico-molybdate

(the existence of which is disputed), may be present. By allowing the ammonia solution to stand for some time after addition of NH_4Cl the flocculent silica separates and may be filtered off.

Fe_2O_3 in the precipitate often causes it to separate in crusts on the sides of the beaker. On attempting to dissolve in ammonia, yellow to red $\text{Fe}_2(\text{OH})_2$, mixed with $\text{Fe}_2(\text{PO})_2$, remains undissolved. After washing with ammonia this residue is dissolved in HNO_3 , the solutions united and reprecipitation effected after acidifying with HNO_3 .

Hydrated TiO_2 (which retains P_2O_5) can be separated by fusing the portion insoluble in ammonia for some time with Na_2CO_3 (*vid.* Na_2TiO_3), leaching with water, and in the water solution reprecipitating with the molybdate reagent.

Silica.

Rem. and Cond.—On adding an excess of mineral acid to a solution containing a silicate, free silicic acid containing indefinite amounts of water is formed, partially or entirely soluble. On evaporation H_2O (of constitution) is removed and insoluble SiO_2 is separated, which may be filtered off after digestion with diluted acid. HCl is the acid most frequently used. When HNO_3 is used, regard must be had to the fact that certain nitrates ($\text{Fe}_2(\text{NO}_3)_2$, etc.) are decomposed at the temperature usually employed to drive out the last portions of the water (110 to 130° C.), and are not readily re-formed by digestion with diluted HNO_3 . The heat is usually maintained until there is no perceptible odor of acid. With H_2SO_4 the heat is continued until fumes of SO_3 are strongly evolved, indicating that H_2SO_4 is the only free acid remaining. If the heat has not been sufficiently prolonged or intense, the separated silica may be flocculent and filters with difficulty, or some may remain soluble.

If the heat has been too high, the conditions may have favored a recombination of silica with the bases, and

consequent soluble silica (analogous to the action by fusion). The temperature which can safely be applied may be put at 110° to 120° .

To remove SiO_2 completely, a second evaporation of the *filtrate* from the first precipitate seems necessary. Evaporation without filtering does not seem to be so effective.

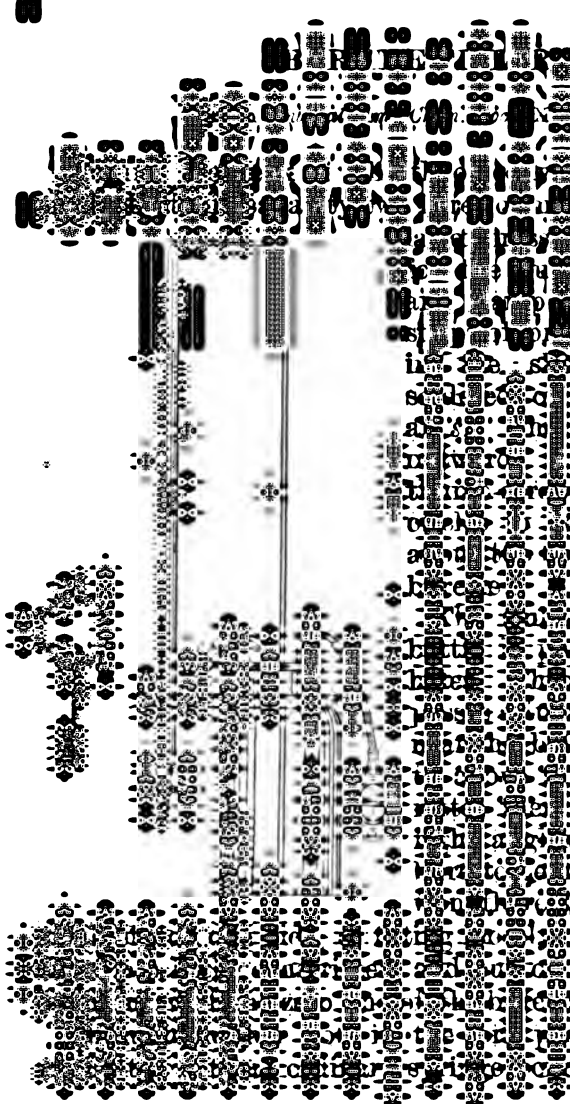
According to Gilbert (*Techn. Quarterly*, February, 1890), when only Ca and alkalies are present, the temperature of drying may be carried up to 280°C . without detriment, but if Mg is present, re-combination of the bases with the silica is best prevented by drying at 120°C . Some alumina almost invariably remains with the silica if Al is present in the solution.

Sol.—Dissolved by boiling or fusing with fixed alkalies, caustic or carbonated. Insoluble in water and acids (HFl excepted).

Contam.—Insoluble sulphates (PbSO_4 , BaSO_4) removed by digestion with conc. H_2SO_4 , and filtering through asbestos. (For other solvents of these substances *vid. sup.*) In some cases CaSO_4 , removable by digestion with HCl and NH_4Cl . The precipitate may also contain a form of $\text{Fe}_2(\text{SO}_4)_3$ (when separated from conc. H_2SO_4) which dissolves in dilute H_2SO_4 with some difficulty, but is readily soluble in HCl.

SnO_2 or Sb_2O_3 may be retained, as well as TiO_2 (possibly combined with P_2O_5) and ferric or aluminic oxides or basic salts. TiO_2 tends to hold P_2O_5 , Al_2O_3 , and Fe_2O_3 in the precipitate. To avoid error in such cases, the SiO_2 should be determined by loss, adding HF or NH_4F , and in any case H_2SO_4 , igniting off SiF_4 and weighing again. This treatment is advisable whenever Al_2O_3 is present in the solution in any quantity.

Ign.—Precipitate is very light and fine, and readily carried off by flame, requiring especial precaution on igniting. After ignition the precipitate will absorb appreciable amounts of water if exposed to air containing moisture.



p. 869.)

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means of which air can be forced into the top of the bottle.

Through the third hole passes another short glass tube, the external end preferably bent downward, so that it may be easily closed by the finger when it may be desired to compress the air in the bottle, or by taking the finger away the pressure may be at once released.

When it is desired to fill the burette, by closing the air-tube with the finger, and squeezing the bulb a few times, the stock solution is forced over into the burette. As soon as the level of the liquid has come to or above the zero-line the air-pressure is released by removing the finger, and all the liquid above the zero-mark siphons back into the stock-bottle, leaving the burette filled to the zero-mark and ready for use.

The device is simple and comparatively inexpensive, and it has the great advantage that the delivery ("nose") of the burette can be easily fixed at a convenient height above the working-table.

TABLES OF WEIGHTS AND MEASURES.

The following comparison of French weights and measures with those of the United States has been taken from tables issued by the United States Coast and Geodetic Survey, Office of Standard Weights and Measures, T. C. Mendenhall, Sup't (1889).

Slight discrepancies from other authorities exist, *e. g.*, the gramme is given by De la Rue as equivalent to 15.4323 grains. The *U. S. Dispensatory*, 13th Ed., pp. 1734 and 1735, gives 15.434 grains, and refers to other authorities which give 15.444 grains as the equivalent of the gramme.

The number of grains in the U. S. gallon of 231 cubic inches is here taken as 58,318, which is believed to be correct, from a calculation based upon results obtained from experimental researches on the expansion of liquids, and a reference to the English standard for the wine or Winchester gallon, on which it is based. (See note of W. H. Chandler, *Am. Chem. I.*, 318.) The *U. S. Dispensatory* (*ib.*) gives 58,328.886 grains.

The report of F. R. Hassler, of the coast survey, gives 58,372.1754 in 1832, and in 1842 Hassler makes it 58,373 grains. The reasons for considering this erroneous will be found in Barnard's *Metric System*, p. 158.

MEASURES OF CAPACITY (U. S. PHARMACOPEIA).

Gal.	Qts.	Pts.	Fl. Oz.	Fl. Dr.	Minims.	Grains of Water at 62° F.	Cubic Centimetres.
1	4	8	= 128	= 1,024	= 61,440	= 58,818.00	= 3,785.430
	1	2	32	256	15,360	14,579.50	946.360
		1	16	128	7,680	7,289.75	473.180
			1	8	480	455.61	29.570
				1	60	56.95	3.700
					1	0.95	0.061
1	English Imperial gallon					= 277.274 cu. in.	70,000.00
1	"	"	pint			34.659 "	8,750.00
<i>Other English gallons :</i>							
1	wine = Winchester gal.					= 231.000 "	58,818.00
1	corn gallon					= 268.800 "	67,861.00
1	ale "					= 262.000 "	71,198.40
1	cu. ft.					= 28.32 litres.	
1	cu. in.					= 16.387 c. c.	

0.061 cu. in. = 1 c. c.

LINEAR MEASURES.

	Metre.		Metre.
1 yard.....	0.91440	1 inch.....	0.0254
1 foot.....	0.30480	39.37 inches.....	1.0000

TROY WEIGHT.

Lb.	Oz.	Dwt.	Grs.	Grammes.
1	12	= 240	= 5,760.....	873.2418
	1	20	480.....	31.1035
		1	24.....	1.5552
			1.....	0.0648

AVOIRDUPOIS WEIGHT.

Gross Ton.Cwt.	Qr.	St.	Lbs.	Kilogrammes.
1	= 20	= 80	= 160 = 2,240.....	1,016.04
	1	4	8	112.....
		1	2	28.....
			1	14.....
				Oz.
				Dr.
				Grs. Troy.
				Grammes.
				1 = 16 = 256 = 7000.00.....
				1 16 437.50.....
				1 27.84.....
1 net ton	= 2,000 lbs.....			29,166½ oz. Troy.....

APOTHECARIES' WEIGHT.

Lb.	Oz.	Dr.	Scruples.	Grains.	Grammes.
1	= 12	= 96	= 288	= 5,760.....	873.2418
	3	1	8	24	480.....
		3	1	3	60.....
			3	1	20.....
0.0022 lb. Av.	= 0.03527 oz. Av.	= 15.43236 grs.....			1 gm.
				Lbs. Av.	Grammes.
1 cu. ft. water at 62° F.	= 62.3550.....				28,320.000
1 cu. in. " " "				0.0361.....	16.387

— *Watts's Dictionary*, V., 1010.

TABLE OF ATOMIC MASSES.

Revised by F. W. CLARKE,

Chief Chemist of the United States Geological Survey.

REVISED TO JAN. 1, 1904.

Name.	Symbol.	Atomic Mass.	Name.	Symbol.	Atomic Mass.
Aluminum.....	Al	27	Neodymium....	Nd	140.5
Antimony.....	Sb	120	Nickel.....	Ni	58.7
Arsenic.....	As	75	Nitrogen.....	N	14.03
Barium.....	Ba	137.43	Osmium.....	Os	190.8
Bismuth.....	Bi	208	Oxygen.....	O	16
Boron.....	*B	11	Palladium.....	Pb	106.5
Bromine.....	Br	79.95	Phosphorus....	*P	31
Cadmium.....	Cd	112	Platinum.....	Pt	195
Cæsium.....	Cs	132.9	Potassium.....	K	39.11
Calcium.....	Ca	40	Præodymium...	Pr	143.5
Carbon.....	C	12	Rhodium.....	Rh	103
Cerium.....	Ce	140.2	Rubidium.....	Rb	85.5
Chlorine.....	Cl	35.45	Ruthenium....	Ru	101.6
Chromium.....	Cr	52.1	Samarium.....	Sm	160
Cobalt.....	Co	59.5	Scandium.....	Sc	44
Columbium.....	†Cb	94	Selenium.....	Se	79
Copper.....	Cu	63.6	Silicon.....	Si	28.4
Erbium.....	Er	166.3	Silver.....	Ag	107.92
Fluorine.....	*F	19	Sodium.....	Na	23.05
Gadolinium....	Gd	156.1	Strontium.....	Sr	87.66
Gallium.....	Ga	69	Sulphur.....	S	32.06
Germanium.....	Ge	72.3	Tantalum.....	Ta	182.6
Glucinum.....	*†G	9	Tellurium.....	Te	125
Gold.....	Au	197.8	Terbium.....	Tb	160
Hydrogen.....	H	1.008	Thallium.....	Tl	204.18
Indium.....	In	113.7	Thorium.....	Th	232.6
Iodine.....	I	126.85	Thulium.....	Tu	170.7
Iridium.....	Ir	193.1	Tin.....	Sn	119
Iron.....	Fe	56	Titanium.....	Ti	48
Lanthanum.....	La	138.2	Tungsten.....	W	184.9
Lead.....	Pb	206.95	Uranium.....	U	239.6
Lithium.....	Li	7.02	Vanadium.....	*V	51.4
Magnesium.....	Mg	24.3	Ytterbium.....	Yb	173
Manganese.....	Mn	55	Yttrium.....	Yt	89.1
Mercury.....	Hg	200	Zinc.....	Zn	65.3
Molybdenum...	Mo	96	Zirconium.....	Zr	90.6

Argon (A = 40) and Helium (He = 4) were not discovered when this table was prepared.

* Symbols sometimes given with a small letter attached : Bo, Fl, Gl, Ph, Vd.

† Sometimes called Niobium, Nb.

‡ Sometimes called Beryllium, Be.

TABLE OF SPECIFIC GRAVITIES CORRESPONDING WITH DEGREES BEAUMÉ FOR
LIQUIDS LIGHTER THAN WATER.

The following is taken from the *United States Dispensatory* (Wood and Bache). In that volume three different values are given for the value of degrees Beaumé in specific gravities. Those which follow were from the French Codex :

Deg. B.	Specific gravity.	Deg. B.	Specific gravity.	Deg. B.	Specific gravity.	Deg. B.	Specific gravity.
10...	1.000	27...	0.894	44...	0.809	61...	0.788
11...	0.998	28...	0.889	45...	0.804	62...	0.785
12...	0.996	29...	0.888	46...	0.800	63...	0.781
13...	0.979	30...	0.878	47...	0.795	64...	0.727
14...	0.978	31...	0.872	48...	0.791	65...	0.724
15...	0.966	32...	0.867	49...	0.787	66...	0.720
16...	0.960	33...	0.862	50...	0.783	67...	0.716
17...	0.958	34...	0.857	51...	0.778	68...	0.713
18...	0.947	35...	0.852	52...	0.774	69...	0.709
19...	0.941	36...	0.847	53...	0.770	70...	0.706
20...	0.935	37...	0.842	54...	0.766	71...	0.702
21...	0.929	38...	0.837	55...	0.762	72...	0.699
22...	0.923	39...	0.832	56...	0.758	73...	0.696
23...	0.917	40...	0.827	57...	0.754	74...	0.692
24...	0.911	41...	0.823	58...	0.750	75...	0.689
25...	0.905	42...	0.818	59...	0.746	76...	0.686
26...	0.900	43...	0.813	60...	0.742	77...	0.682

The specific gravity may be calculated from the formula :

$$\text{Sp. gr.} = \frac{144}{B + 134}.$$

For specific gravities corresponding with degrees B. for liquids heavier than water, see Table of values of Sulphuric acid.

VALUES OF SULPHURIC ACID.

Table adopted by the Manufacturing Chemists' Association of the United States, March, 1882.

The standards adopted are :

The Beaumé hydrometer with a modulus of 145.

$$\text{Sp. Gr.} = \frac{145}{145 - \text{Bé.}^\circ}$$

$$0^\circ \text{ Bé} = \text{Sp. Gr. 1.000.} \quad 66^\circ \text{ Bé.} = \text{Sp. Gr. 1.835 at } 60^\circ \text{ Fahr.}$$

"O. V." is the abbreviation for oil of vitriol containing 98.5 per cent H_2SO_4 .

One cubic foot of water weighs 62.37 lbs. Av.

"Tw." signifies degrees Twaddell, a scale used by English manufacturers. Degrees Tw. multiplied by 5, and the product added to 1000, gives the Sp. Gr. referred to water as 1000°; e.g.,

$$1^\circ \text{ Tw.} = \text{Sp. Gr. 1.005,} \quad 28^\circ \text{ Tw.} = 1.115, \text{ etc.}$$

Bé. Deg.	Sp. Gr.	Weight of 1 Cu. Ft. in Lbs. Av.	Per Cent O. V.	Pounds O. V. in 1 Cu. Ft.	Tw. Deg.	Per Cent H_2SO_4 .
0	1.000	62.37	0.00	0.00	0	0.000
1	1.007	62.81	1.00	0.63	1½	0.935
2	1.014	63.24	2.50	1.58	3	2.337
3	1.021	63.68	3.66	2.33	4	3.422
4	1.028	64.12	5.00	3.21	5½	4.675
5	1.036	64.62	6.00	3.88	7	5.610
6	1.043	65.05	7.00	4.55	8½	6.545
7	1.051	65.55	8.00	5.24	10	7.480
8	1.058	65.99	9.00	5.94	11½	8.415
9	1.066	66.49	10.25	6.82	13	9.584
10	1.074	66.99	11.50	7.70	15	10.752
11	1.082	67.48	12.50	8.44	16½	11.687
12	1.090	67.98	13.60	9.25	18	12.716
13	1.098	68.48	14.70	10.07	19½	13.744
14	1.107	69.04	16.00	11.05	21½	14.960
15	1.115	69.54	17.00	11.82	23	15.895
16	1.124	70.10	18.25	12.79	25	17.064
17	1.133	70.67	19.60	13.85	26½	18.326
18	1.142	71.23	21.00	14.96	28½	19.635
19	1.151	71.79	22.00	15.79	30	20.570
20	1.160	72.35	23.25	16.82	32	21.739
21	1.169	72.91	24.50	17.86	34	22.907
22	1.179	73.53	26.00	19.12	36	24.310
23	1.188	74.10	27.25	20.19	37½	25.479
24	1.198	74.72	28.50	21.30	39½	26.647
25	1.208	75.34	30.00	22.60	41½	28.050

Bé. Deg.	Sp. Gr.	Weight of 1 Cu. Ft. in Lbs. Av.	Per Cent O. V.	Pounds O. V. in 1 Cu. Ft.	Tw. Deg.	Per Cent H ₂ SO ₄ .
26	1.218	75.97	31.25	28.74	43½	29.219
27	1.229	76.65	32.75	25.10	46	30.621
28	1.239	77.28	34.00	26.28	48	31.790
29	1.250	77.96	35.50	27.68	50	33.192
30	1.261	78.65	37.00	29.10	52	34.595
31	1.272	79.33	38.37	30.44	54½	35.876
32	1.283	80.02	39.75	31.81	56½	37.166
33	1.295	80.77	41.25	33.32	59	38.569
34	1.306	81.46	42.62	34.72	61	39.850
35	1.318	82.20	44.00	36.17	63½	41.140
36	1.330	82.95	45.50	37.74	66	42.542
37	1.342	83.70	47.00	39.34	68½	43.945
38	1.355	84.51	48.50	40.99	71	45.347
39	1.368	85.32	50.00	42.66	73½	46.750
40	1.381	86.13	51.50	44.36	76	48.152
41	1.394	86.94	53.00	46.08	79	49.555
42	1.408	87.82	54.50	47.86	81½	50.957
43	1.421	88.63	56.00	49.63	84	52.360
44	1.436	89.56	57.50	51.50	87	53.762
45	1.450	90.44	59.00	53.36	90	55.165
46	1.465	91.37	60.50	55.28	93	56.567
47	1.479	92.25	62.00	57.20	96	57.970
48	1.495	93.24	63.50	59.21	99	59.372
49	1.510	94.18	65.00	61.22	102	60.775
50	1.526	95.18	66.50	63.29	105	62.177
51	1.542	96.17	68.00	65.40	108½	63.580
52	1.559	97.23	69.70	67.77	112	65.169
53	1.576	98.30	71.30	70.09	115	66.665
54	1.593	99.36	73.00	72.53	118½	68.255
55	1.611	100.48	74.60	74.96	122	69.751
56	1.629	101.60	76.20	77.42	126	71.247
57	1.648	102.79	77.87	80.04	129½	72.808
58	1.666	103.91	79.50	82.61	133	74.332
59	1.686	105.16	81.30	85.50	137	76.015
60	1.706	106.40	83.00	88.81	141	77.605
61	1.726	107.65	85.00	91.50	145	79.475
62	1.747	108.96	87.00	94.80	149½	81.345
63	1.768	110.27	89.00	98.14	153½	83.215
64	1.790	111.64	91.62	102.29	158	85.665
½						
½	1.801	112.33	93.12	104.60	160½	87.067
½	1.807	112.70	94.00	105.94	161½	87.890
65	1.812	113.01	94.70	107.02	162½	88.544
½	1.818	113.39	95.66	108.47	163½	89.442
½	1.824	113.76	96.80	110.12	164½	89.50
½	1.830	114.14	98.33	112.23	166	91.939
66	1.835	114.45	100.00	114.45	167	93.500

TABLE OF SPECIFIC GRAVITY OF SOLUTIONS OF HYDROCHLORIC ACID. TEMP.,
15° (URE).

Specific gravity.	Per cent HCl.	Specific gravity.	Per cent HCl.	Specific gravity.	Per cent HCl.
1.2000	40.777	1.1828	26.918	1.0687	18.049
1.1982	40.869	1.1808	26.505	1.0617	12.641
1.1964	39.961	1.1287	26.098	1.0597	12.233
1.1946	39.554	1.1267	25.690	1.0577	11.825
1.1928	39.146	1.1247	25.282	1.0557	11.418
1.1910	38.738	1.1226	24.874	1.0537	11.010
1.1893	38.330	1.1206	24.466	1.0517	10.602
1.1875	37.922	1.1185	24.058	1.0497	10.194
1.1857	37.516	1.1164	23.650	1.0477	9.786
1.1846	37.108	1.1143	23.242	1.0457	9.379
1.1822	36.700	1.1123	22.834	1.0437	8.971
1.1802	36.292	1.1102	22.426	1.0417	8.563
1.1782	35.884	1.1082	22.019	1.0397	8.155
1.1762	35.476	1.1061	21.611	1.0377	7.747
1.1741	35.068	1.1041	21.208	1.0357	7.340
1.1721	34.660	1.1020	20.796	1.0337	6.932
1.1701	34.252	1.1000	20.388	1.0318	6.524
1.1681	33.845	1.0980	19.980	1.0298	6.116
1.1661	33.437	1.0960	19.572	1.0279	5.709
1.1641	33.029	1.0939	19.165	1.0259	5.301
1.1620	32.621	1.0919	18.757	1.0239	4.893
1.1599	32.213	1.0899	18.349	1.0220	4.486
1.1578	31.805	1.0879	17.941	1.0200	4.078
1.1557	31.398	1.0857	17.534	1.0180	3.670
1.1537	30.990	1.0838	17.126	1.0160	3.262
1.1515	30.582	1.0818	16.718	1.0140	2.854
1.1494	30.174	1.0798	16.310	1.0120	2.447
1.1472	29.767	1.0778	15.902	1.0100	2.039
1.1452	29.359	1.0758	15.494	1.0080	1.631
1.1431	28.951	1.0738	15.087	1.0060	1.124
1.1410	28.544	1.0718	14.679	1.0040	0.816
1.1389	28.136	1.0697	14.271	1.0020	0.408
1.1369	27.728	1.0677	13.863		
1.1349	27.321	1.0657	13.456		

TABLE SHOWING THE AMOUNT OF NITRIC ACID (HNO_3) CONTAINED IN SOLUTIONS OF DIFFERENT SPECIFIC GRAVITIES. TEMP., 15° (URE).

HNO_3 per cent.	Specific gravity.	HNO_3 per cent.	Specific gravity.	HNO_3 per cent.	Specific gravity.
100.	1.5000	66.	1.3788	38.	1.1895
99.	1.4980	65.	1.3782	37.	1.1883
98.	1.4960	64.	1.3681	31.	1.1770
97.	1.4940	63.	1.3680	30.	1.1709
96.	1.4910	62.	1.3579	29.	1.1648
95.	1.4880	61.	1.3529	28.	1.1587
94.	1.4850	60.	1.3477	27.	1.1526
93.	1.4820	59.	1.3427	26.	1.1465
92.	1.4790	58.	1.3376	25.	1.1403
91.	1.4760	57.	1.3328	24.	1.1345
90.	1.4730	56.	1.3270	23.	1.1286
89.	1.4700	55.	1.3216	22.	1.1227
88.	1.4670	54.	1.3168	21.	1.1168
87.	1.4640	53.	1.3110	20.	1.1109
86.	1.4600	52.	1.3056	19.	1.1051
85.	1.4570	51.	1.3001	18.	1.0998
84.	1.4530	50.	1.2947	17.	1.0935
83.	1.4500	49.	1.2887	16.	1.0878
82.	1.4460	48.	1.2826	15.	1.0821
81.	1.4424	47.	1.2765	14.	1.0764
80.	1.4385	46.	1.2705	13.	1.0708
79.	1.4346	45.	1.2644	12.	1.0651
78.	1.4306	44.	1.2583	11.	1.0595
77.	1.4269	43.	1.2523	10.	1.0540
76.	1.4228	42.	1.2462	9.	1.0485
75.	1.4189	41.	1.2402	8.	1.0430
74.	1.4147	40.	1.2341	7.	1.0375
73.	1.4107	39.	1.2277	6.	1.0320
72.	1.4065	38.	1.2212	5.	1.0267
71.	1.4023	37.	1.2148	4.	1.0212
70.	1.3978	36.	1.2084	3.	1.0159
69.	1.3945	35.	1.2019	2.	1.0106
68.	1.3882	34.	1.1958	1.	1.0053
67.	1.3883				

TABLE OF SPECIFIC GRAVITY OF SOLUTIONS OF CRYSTALLIZED TARTARIC ACID IN WATER. TEMP., 15°. WATER AT 15° = 1.

GERLACH, "SPECIFISCHE GEWICHTE DER SAZELÖSUNGEN."					
Per cent.	Specific gravity.	Per cent.	Specific gravity.	Per cent.	Specific gravity.
1.....	1.00450	20.....	1.09698	39.....	1.20190
2.....	1.00900	21.....	1.10200	40.....	1.20785
3.....	1.01360	22.....	1.10720	41.....	1.21380
4.....	1.01790	23.....	1.11240	42.....	1.21980
5.....	1.02240	24.....	1.11750	43.....	1.22590
6.....	1.02730	25.....	1.12270	44.....	1.23170
7.....	1.03220	26.....	1.12820	45.....	1.23770
8.....	1.03710	27.....	1.13380	46.....	1.24410
9.....	1.04200	28.....	1.13980	47.....	1.25040
10.....	1.04692	29.....	1.14490	48.....	1.25680
11.....	1.05170	30.....	1.15047	49.....	1.26320
12.....	1.05650	31.....	1.15600	50.....	1.26962
13.....	1.06130	32.....	1.16150	51.....	1.27620
14.....	1.06620	33.....	1.16700	52.....	1.28280
15.....	1.07090	34.....	1.17260	53.....	1.28940
16.....	1.07610	35.....	1.17810	54.....	1.29610
17.....	1.08130	36.....	1.18400	55.....	1.30270
18.....	1.08650	37.....	1.19000	56.....	1.30980
19.....	1.09170	38.....	1.19690	57.....	1.31590

TABLE OF SPECIFIC GRAVITY OF SOLUTIONS OF CRYSTALLIZED CITRIC ACID IN WATER. TEMP., 15°. WATER AT 15° = 1.

GERLACH, "SPECIFISCHE GEWICHTE DER SAZELÖSUNGEN."					
Per cent.	Specific gravity.	Per cent.	Specific gravity.	Per cent.	Specific gravity.
1.....	1.00370	23.....	1.09800	45.....	1.19470
2.....	1.00740	24.....	1.09720	46.....	1.19980
3.....	1.01110	25.....	1.10140	47.....	1.20500
4.....	1.01490	26.....	1.10600	48.....	1.21030
5.....	1.01860	27.....	1.11060	49.....	1.21580
6.....	1.02270	28.....	1.11520	50.....	1.22041
7.....	1.02680	29.....	1.11980	51.....	1.22570
8.....	1.03090	30.....	1.12439	52.....	1.23070
9.....	1.03500	31.....	1.12880	53.....	1.23590
10.....	1.03916	32.....	1.13330	54.....	1.24100
11.....	1.04310	33.....	1.13780	55.....	1.24620
12.....	1.04700	34.....	1.14220	56.....	1.25140
13.....	1.05090	35.....	1.14670	57.....	1.25720
14.....	1.05490	36.....	1.15150	58.....	1.26270
15.....	1.05880	37.....	1.15640	59.....	1.26830
16.....	1.06320	38.....	1.16120	60.....	1.27382
17.....	1.06750	39.....	1.16610	61.....	1.27940
18.....	1.07180	40.....	1.17093	62.....	1.28490
19.....	1.07620	41.....	1.17560	63.....	1.29040
20.....	1.08052	42.....	1.18140	64.....	1.29600
21.....	1.08480	43.....	1.18510	65.....	1.30150
22.....	1.08890	44.....	1.18990	66.....	1.30710

TABLE OF SPECIFIC GRAVITY OF SOLUTIONS OF ACETIC ACID. TEMP., 15°.

C ₂ H ₄ O ₂ per cent.	Specific gravity.	C ₂ H ₄ O ₂ per cent.	Specific gravity.	C ₂ H ₄ O ₂ per cent.	Specific gravity.	C ₂ H ₄ O ₂ per cent.	Specific gravity.
0...	1.0000	26..	1.0868	51..	1.0638	76..	1.0747
1...	1.0007	27..	1.0875	52..	1.0631	77..	1.0748
2...	1.0022	28..	1.0888	53..	1.0638	78..	1.0748
3...	1.0087	29..	1.0400	54..	1.0646	79..	1.0748
4...	1.0053	30..	1.0412	55..	1.0653	80..	1.0748
5...	1.0067	31..	1.0424	56..	1.0660	81..	1.0747
6...	1.0068	32..	1.0436	57..	1.0666	82..	1.0746
7...	1.0098	33..	1.0447	58..	1.0673	83..	1.0744
8...	1.0118	34..	1.0459	59..	1.0679	84..	1.0742
9...	1.0127	35..	1.0470	60..	1.0685	85..	1.0739
10...	1.0142	36..	1.0481	61..	1.0691	86..	1.0736
11...	1.0157	37..	1.0492	62..	1.0697	87..	1.0731
12...	1.0171	38..	1.0502	63..	1.0703	88..	1.0726
13...	1.0185	39..	1.0513	64..	1.0707	89..	1.0720
14...	1.0201	40..	1.0523	65..	1.0712	90..	1.0718
15...	1.0214	41..	1.0533	66..	1.0717	91..	1.0705
16...	1.0228	42..	1.0543	67..	1.0721	92..	1.0696
17...	1.0242	43..	1.0552	68..	1.0725	93..	1.0688
18...	1.0256	44..	1.0562	69..	1.0729	94..	1.0674
19...	1.0270	45..	1.0571	70..	1.0733	95..	1.0660
20...	1.0284	46..	1.0580	71..	1.0737	96..	1.0644
21...	1.0298	47..	1.0589	72..	1.0740	97..	1.0625
22...	1.0311	48..	1.0598	73..	1.0742	98..	1.0604
23...	1.0324	49..	1.0607	74..	1.0744	99..	1.0580
24...	1.0337	50..	1.0615	75..	1.0746	100..	1.0553
25...	1.0350						

TABLE SHOWING THE PERCENTAGE OF AMMONIA (NH₃) CONTAINED IN SOLUTIONS OF DIFFERENT SPECIFIC GRAVITIES. TEMP., 14° (CARIUS).

Specific gravity.	Am- monia, per cent.	Specific gravity.	Am- monia, per cent.	Specific gravity.	Am- monia, per cent.	Specific gravity.	Am- monia, per cent.
0.8844	36	0.9052	27	0.9814	18	0.9631	9
0.8864	35	0.9078	26	0.9847	17	0.9670	8
0.8885	34	0.9106	25	0.9880	16	0.9709	7
0.8907	33	0.9133	24	0.9414	15	0.9749	6
0.8929	32	0.9162	23	0.9449	14	0.9790	5
0.8953	31	0.9191	22	0.9484	13	0.9831	4
0.8976	30	0.9221	21	0.9520	12	0.9873	3
0.9001	29	0.9251	20	0.9556	11	0.9915	2
0.9024	28	0.9283	19	0.9593	10	0.9959	1

TABLE SHOWING THE AMOUNT OF K_2O IN POTASSA LYE OF DIFFERENT SPECIFIC GRAVITIES. TEMP., 17.5° .

HOFFMAN, SCHAEDLER, "TABELLEN FÜR CHEMIKER." P. 119.

K_2O per cent.	Specific gravity.	K_2O per cent.	Specific gravity.	K_2O per cent.	Specific gravity.	K_2O per cent.	Specific gravity.
45.	1.576	34.	1.414	28.	1.269	12.	1.185
44.5	1.568	33.5	1.407	22.5	1.263	11.5	1.129
44.	1.560	33.	1.400	22.	1.257	11.	1.123
43.5	1.553	32.5	1.393	21.5	1.250	10.5	1.117
43.	1.545	32.	1.386	21.	1.244	10.	1.111
42.5	1.537	31.5	1.379	20.5	1.238	9.5	1.105
42.	1.530	31.	1.372	20.	1.231	9.	1.099
41.5	1.522	30.5	1.365	19.5	1.225	8.5	1.094
41.	1.514	30.	1.358	19.	1.219	8.	1.088
40.5	1.507	29.5	1.352	18.5	1.213	7.5	1.082
40.	1.500	29.	1.345	18.	1.207	7.	1.076
39.5	1.492	28.5	1.339	17.5	1.201	6.5	1.070
39.	1.484	28.	1.332	17.	1.195	6.	1.065
38.5	1.477	27.5	1.326	16.5	1.189	5.5	1.059
38.	1.470	27.	1.320	16.	1.183	5.	1.054
37.5	1.463	26.5	1.313	15.5	1.177	4.5	1.048
37.	1.456	26.	1.307	15.	1.171	4.	1.042
36.5	1.449	25.5	1.301	14.5	1.165	3.5	1.037
36.	1.442	25.	1.294	14.	1.159	3.	1.031
35.5	1.435	24.5	1.288	13.5	1.153	2.5	1.026
35.	1.428	24.	1.282	13.	1.147	2.	1.021
34.5	1.421	23.5	1.275	12.5	1.141	1.5	1.015

TABLE SHOWING THE SODIUM OXIDE (Na_2O) IN SODA LYES OF DIFFERENT SPECIFIC GRAVITIES. TEMP., 17.5° .

HOFFMAN-SCHAEDLER, "TABELLEN FÜR CHEMIKER."

Na_2O per cent.	Specific gravity.	Na_2O per cent.	Specific gravity.	Na_2O per cent.	Specific gravity.	Na_2O per cent.	Specific gravity.
35.	1.500	27.5	1.389	20.	1.281	12.5	1.174
34.5	1.492	27.	1.382	19.5	1.274	12.	1.167
34.	1.485	26.5	1.375	19.	1.276	11.5	1.160
33.5	1.477	26.	1.367	18.5	1.259	11.	1.153
33.	1.470	25.5	1.360	18.	1.252	10.5	1.146
32.5	1.463	25.	1.353	17.5	1.245	10.	1.139
32.	1.455	24.5	1.345	17.	1.238	9.5	1.132
31.5	1.448	24.	1.338	16.5	1.231	9.	1.125
31.	1.440	23.5	1.331	16.	1.224	8.5	1.118
30.5	1.433	23.	1.324	15.5	1.217	8.	1.111
30.	1.426	22.5	1.317	15.	1.210	7.5	1.104
29.5	1.418	22.	1.309	14.5	1.203	7.	1.097
29.	1.411	21.5	1.302	14.	1.195	6.5	1.090
28.5	1.404	21.	1.295	13.5	1.188	6.	1.083
28.	1.396	20.5	1.288	13.	1.181	5.5	1.076

TABLE OF SPECIFIC GRAVITY OF SOLUTIONS OF SODIUM CHLORIDE AT 15°. WATER AT 15° = 1.

GERLACH, "SPECIFISCHE GEWICHTE DER SALZLÖSUNGEN."			
Per cent.	Specific gravity.	Per cent.	Specific gravity.
1.....	1.00725	14.....	1.10384
2.....	1.01450	15.....	1.11146
3.....	1.02174	16.....	1.11908
4.....	1.02899	17.....	1.12780
5.....	1.03624	18.....	1.13533
6.....	1.04366	19.....	1.14315
7.....	1.05108	20.....	1.15107
8.....	1.05851	21.....	1.15981
9.....	1.06598	22.....	1.16755
10.....	1.07335	23.....	1.17580
11.....	1.08097	24.....	1.18404
12.....	1.08859	25.....	1.19238
13.....	1.09622	26.....	1.20098

TABLE SHOWING THE PERCENTAGE OF AMMONIUM CHLORIDE IN SOLUTIONS OF DIFFERENT SPECIFIC GRAVITIES. TEMP., 15°. WATER AT 15° = 1.

GERLACH, "SPECIFISCHE GEWICHTE DER SALZLÖSUNGEN."			
Per cent.	Specific gravity.	Per cent.	Specific gravity.
1.....	1.00816	14.....	1.04325
2.....	1.00632	15.....	1.04524
3.....	1.00948	16.....	1.04805
4.....	1.01264	17.....	1.05086
5.....	1.01580	18.....	1.05367
6.....	1.01880	19.....	1.05648
7.....	1.02180	20.....	1.05929
8.....	1.02481	21.....	1.06204
9.....	1.02781	22.....	1.06479
10.....	1.03081	23.....	1.06754
11.....	1.03370	24.....	1.07029
12.....	1.03653	25.....	1.07304
13.....	1.03947	26.....	1.07575

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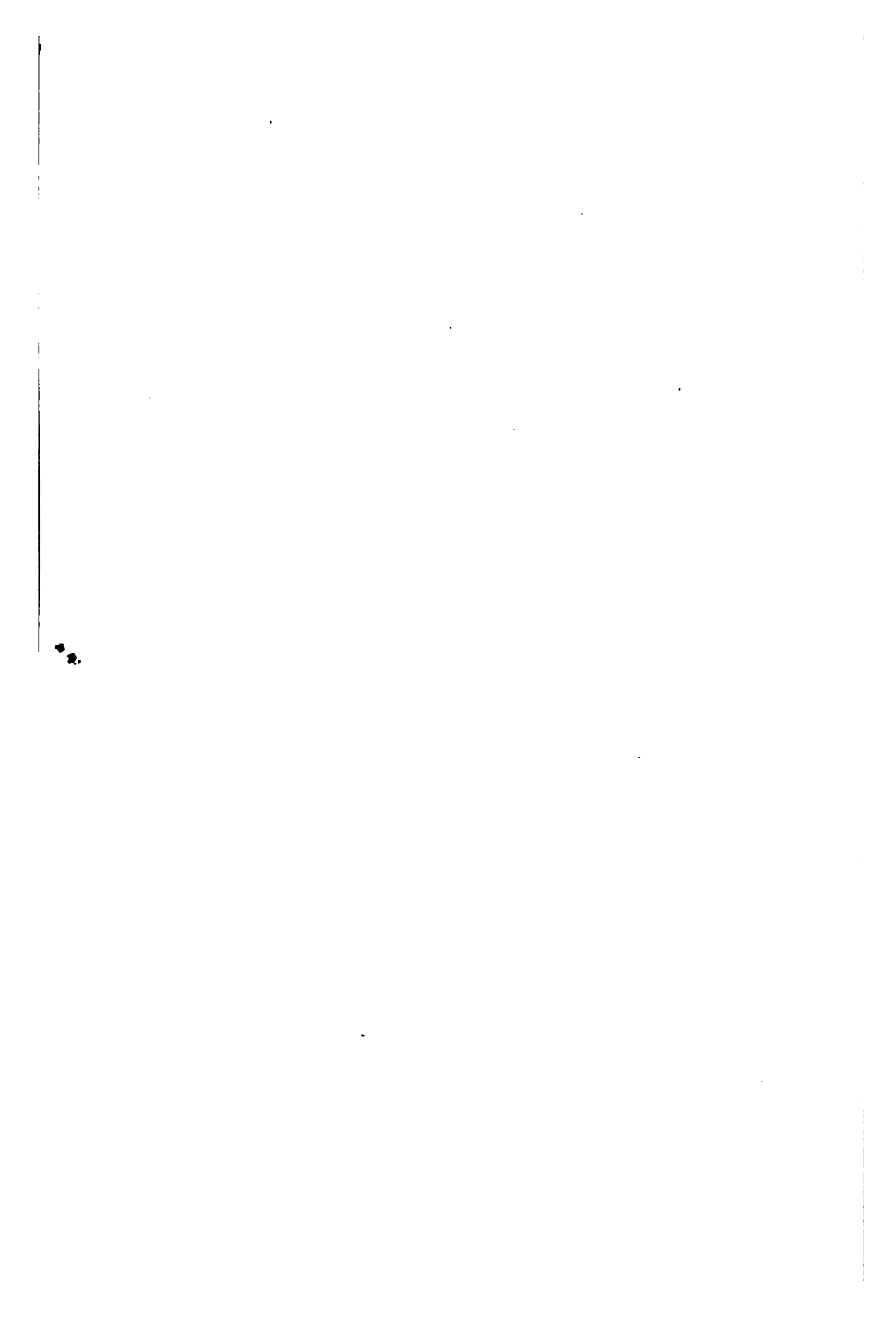
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